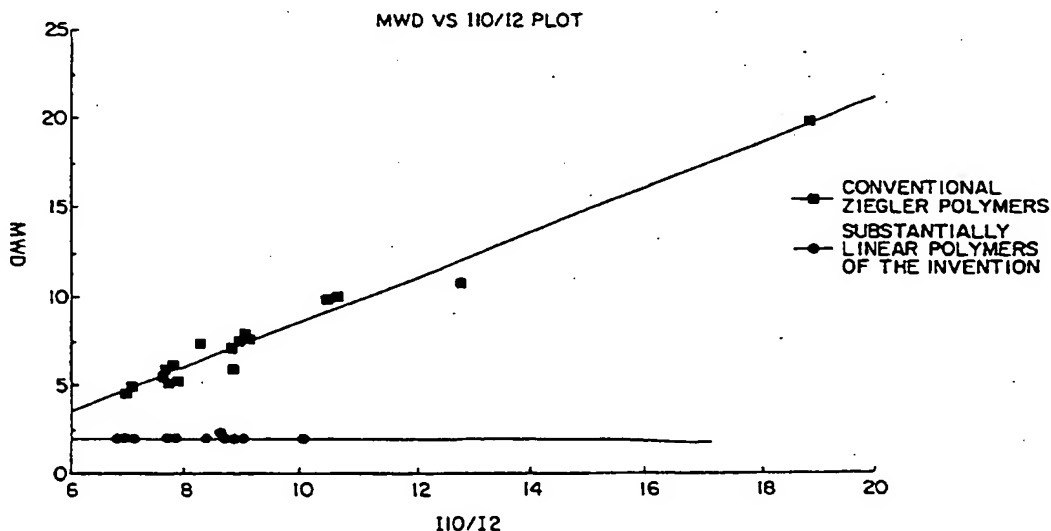| (51) International Patent Classification 6 : C08F 210/16, 4/603, C08L 23/04, C08J 5/18	A1	(11) International Publication Number: **WO 96/07680** (43) International Publication Date: 14 March 1996 (14.03.96)

(21) International Application Number: PCT/US95/11034

(22) International Filing Date: 29 August 1995 (29.08.95)

(30) Priority Data:
08/301,948   7 September 1994 (07.09.94)   US

(60) Parent Application or Grant
(63) Related by Continuation
US   08/301,948 (CIP)
Filed on   7 September 1994 (07.09.94)

(71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).

(72) Inventors; and
(75) Inventors/Applicants (for US only): LAI, Shih-Yaw [US/US]; 4523 Bermuda Drive, Sugar Land, TX 77479 (US). WILSON, John, R. [US/US]; 14523 North Majestic Oak Place, Baton Rouge, LA 70810 (US). KNIGHT, George, W. [US/US]; 1618 North Road, Lake Jackson, TX 77566 (US). STEVENS, James, C. [US/US]; 2026 Pecan Trail Drive, Richmond, TX 77469 (US). CHUM, Pak-Wing, S. [US/US]; 126 Juniper, Lake Jackson, TX 77566 (US).

(74) Agent: KRUPP, Stephen, P.; The Dow Chemical Company, Patent Dept., Building B-1211, Freeport, TX 77541-3257 (US).

(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PLASTIC LINEAR LOW DENSITY POLYETHYLENE

(57) Abstract

Elastic ethylene polymers are disclosed which have processability similar to highly branched low density polyethylene (LDPE), but the strength and toughness of linear low density polyethylene (LLDPE). The polymers have processing indices (PI's) less than or equal to 70 percent of those of a comparative linear ethylene polymer and a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a traditional linear ethylene polymer at about the same I_2, density and M_w/M_n. The novel polymers can also have from 0.01 to 3 long chain branches/1000 total carbons and have higher low/zero shear viscosity and lower high shear viscosity than comparative linear ethylene polymers. The novel polymers can also be characterized as having a melt flow ratio, I_{10}/I_2, $\geq$ 5.63, a molecular weight distribution, M_w/M_n, defined by the equation: $M_w/M_n \leq (I_{10}/I_2) - 4.63$, a critical shear stress at onset of gross melt fracture greater than 4×10^6 dyne/cm^2, and a single DSC melt peak between -30 °C and 150 °C.

Plastic linear low density polyethylene.

This invention relates to elastic substantially linear ethylene polymers having improved processability, for example, low susceptibilty to melt fracture, even under high shear stress conditions. Such substantially linear ethylene polymers have a critical shear
5   rate at the onset of surface melt fracture substantially higher than, and a processing index substantially less than, that of a linear polyethylene at the same molecular weight distribution and melt index.

Molecular weight distribution (MWD), or polydispersity, is a well known variable in polymers. The molecular weight distribution, sometimes described as the ratio of weight
10   average molecular weight (M_w) to number average molecular weight (M_n) (that is, M_w/M_n) can be measured directly, for example, by gel permeation chromatography techniques, or more routinely, by measuring I_{10}/I_2 ratio, as described in ASTM D-1238. For linear polyolefins, especially linear polyethylene, it is well known that as M_w/M_n increases, I_{10}/I_2 also increases.

15   John Dealy in "Melt Rheology and Its Role in Plastics Processing" (Van Nostrand Reinhold, 1990) page 597 discloses that ASTM D-1238 is employed with different loads in order to obtain an estimate of the shear rate dependence of melt viscosity, which is sensitive to weight average molecular weight (M_w) and number average molecular weight (M_n).

20   Bersted in Journal of Applied Polymer Science Vol. 19, page 2167-2177 (1975) theorized the relationship between molecular weight distribution and steady shear melt viscosity for linear polymer systems. He also showed that the broader MWD material exhibits a higher shear rate or shear stress dependency.

Ramamurthy in Journal of Rheology, 30(2), 337-357 (1986), and Moynihan, Baird
25   and Ramanathan in Journal of Non-Newtonian Fluid Mechanics, 36, 255-263 (1990), both disclose that the onset of sharkskin (that is, surface melt fracture) for linear low density polyethylene (LLDPE) occurs at an apparent shear stress of 1-1.4 x 10^6 dyne/cm^2, which was observed to be coincident with the change in slope of the flow curve. Ramamurthy also discloses that the onset of surface melt fracture or of gross melt fracture for high pressure
30   low density polyethylene (HP-LDPE) occurs at an apparent shear stress of about 0.13 MPa (1.3 x 10^6 dyne/cm^2). Ramamurthy also discloses that "the corresponding shear stresses (0.14 and 0.43 MPa) for linear polyethylenes are widely separated." However, these LLDPE resins are linear resins, and are believed to be those made by Union Carbide in their UNIPOL process (which uses conventional Ziegler-Natta catalysis which results in a
35   heterogeneous comonomer distribution). The LLDPE is reported in Tables I and II to have a broad M_w/M_n of 3.9. The melt fracture tests conducted by Ramamurthy were in the temperature range of 190 to 220°C. Furthermore, Ramamurthy reports that the onset of both surface and gross melt fracture (for LLDPE resins) are ". . . essentially independent of MI (or

molecular weight), melt temperature, die diameter (0.5-2.5 mm), die length/diameter ratio (2-20), and the die entry angle (included angle: 60-180 degrees)."

Kalika and Denn in Journal of Rheology, 31, 815-834 (1987) confirmed the surface defects or sharkskin phenomena for LLDPE, but the results of their work determined a critical shear stress at onset of surface melt fracture of 0.26 MPa, significantly higher than that found by Ramamurthy and Moynihan et al. Kalika and Denn also report that the onset of gross melt fracture occurs at 0.43 MPa which is consistent with that reported by Ramamurthy. The LLDPE resin tested by Kalika and Denn was an antioxidant-modified (of unknown type) UNIPOL LLDPE having a broad M_w/M_n of 3.9. Kalika and Denn performed their melt fracture tests at 215°C. However, Kalika and Denn seemingly differ with Ramamurthy in the effects of their L/D of the rheometer capillary. Kalika and Denn tested their LLDPE at L/D's of 33.2, 66.2, 100.1, and 133.1 (see Table 1 and Figures 5 and 6).

International Patent Application (Publication No. WO 90/03414) published April 5, 1990 to Exxon Chemical Company, discloses linear ethylene interpolymer blends with narrow molecular weight distribution and narrow short chain branching distributions (SCBDs). The melt processibility of the interpolymer blends is controlled by blending different molecular weight interpolymers having different narrow molecular weight distributions and different SCBDs.

Exxon Chemical Company, in the Preprints of Polyolefins VII International Conference, page 45-66, February 24-27 1991, disclose that the narrow molecular weight distribution (NMWD) resins produced by their EXXPOL^{TM} technology have higher melt viscosity and lower melt strength than conventional Ziegler resins at the same melt index. In a recent publication, Exxon Chemical Company has also taught that NMWD polymers made using a single site catalyst create the potential for melt fracture ("New Specialty Linear Polymers (SLP) For Power Cables," by Monica Hendewerk and Lawrence Spenadel, presented at IEEE meeting in Dallas, Texas, September, 1991). In a similar vein, in "A New Family of Linear Ethylene Polymers Provides Enhanced Sealing Performance" by Dirk G. F. Van der Sanden and Richard W. Halle, (February 1992 Tappi Journal), Exxon Chemical Company has also taught that the molecular weight distribution of a polymer is described by the polymers melt index ratio (that is, I_{10}/I_2) and that their new narrow molecular weight distribution polymers made using a single site catalyst are "linear backbone resins containing no functional or long chain branches."

USP 5,218,071 (Canadian patent application 2,008,315-A) to Mitsui Petrochemical Industries, Ltd., teaches ethylene copolymers composed of structural units (a) derived from ethylene and structural units (b) derived from alpha-olefins of 3-20 carbons atoms, said ethylene copolymers having [A] a density of 0.85 - 0.92 g/cm^3, [B] an intrinsic viscosity as measured in decalin at 135°C of 0.1 - 10 dl/g, [C] a ratio (M_w/M_n) of a weight average molecular weight (M_w) to a number average molecular weight (M_n) as measured by GPC of

-2-

1.2-4, and [D] a ratio (MFR_{10}/MFR_2) of MFR_{10} under a load of 10 kg to MFR_2 under a load of 2.16 kg at 190°C of 8-50, and beign narrow in molecular weight distribution and excellent in flowability. However, the ethylene copolymers of USP '071 are made with a catalysis system composed of methylaluminoxane and ethylenebis(indenyl)hafnium dichloride

5   (derived from $HfCl_4$ containing 0.78 percent by weight of zirconium atoms as contaminates). It is well known that mixed metal atom catalyst species (such as hafnium and zirconium in USP '071) polymerizes copolymer blends, which are evidenced by multiple melting peaks. Such copolymer blends therefore are not homogeneous in terms of their branching distribution.

10   WO 85/04664 to BP Chemicals Ltd. teaches a process for the thermo-mechanical treatment of copolymers of ethylene and higher alpha-olefins of the linear low density polyethylene type with at least one or more organic peroxides to produce copolymers that are particularly well suited for extrusion or blow-molding into hollow bodies and sheathing. These treated copolymers show an increased flow parameter (I_{21}/I_2) without

15   significantly increasing the M_w/M_n. However, the novel polymers of the present invention have long chained branching and obtained this desirable result without the need of a peroxide treatment.

U. S. Patent 5,096,867 discloses various ethylene polymers made using a single site catalyst in combinations with methyl aluminoxane. These polymers, in particular Example

20   47, have extremely high levels of aluminum resulting from catalyst residue. When these aluminum residues are removed from the polymer, the polymer exhibits gross melt fracture at a critical shear stress of less than 4×10^6 dyne/cm^2.

Previously known narrow molecular weight distribution linear polymers disadvantageously possessed low shear sensitivity or low I_{10}/I_2 value, which limits the

25   extrudability of such polymers. Additionally, such polymers possessed low melt elasticity, causing problems in melt fabrication such as film forming processes or blow molding processes (for example, sustaining a bubble in the blown film process, or sag in the blow molding process etc.). Finally, such resins also experienced melt fracture surface properties at relatively low extrusion rates thereby processing unacceptably.

30   A new class of homogeneous ethylene polymers have now been discovered which have long chain branching and unusual but desirable bulk properties. These new polymers include both homopolymers of ethylene and interpolymers of ethylene and at least one alpha-olefin. Both the homo- and interpolymers have long chain branching, but the interpolymers have short chain branching in addition to the long chain branching. The

35   short chain branches are the residue of the alpha-olefins that are incorporated into the polymer backbone or in other words, the short chain branches are that part of the alpha-olefin not incorporated into the polymer backbone. The length of the short chain branches is two carbon atoms less than the length of the alpha-olefin comonomer. The short chain branches are randomly, that is uniformly, distributed throughout the polymer as opposed

-3-

to heterogeneously branched ethylene/alpha-olefin interpolymers such as conventional Ziegler LLDPE.

These novel ethylene polymers have a shear thinning and ease of processability similar to highly branched low density polyethylene (LDPE), but with the strength and toughness of linear low density polyethylene (LLDPE). These novel ethylene polymers can also be characterized as "substantially linear" polymers, whereby the bulk polymer has an average of up to about 3 long chain branches/1000 total carbons or in other words, at least some of the polymer chains have long chain branching. The novel substantially linear ethylene polymers are distinctly different from traditional Ziegler polymerized heterogeneous polymers (for example, LLDPE) and are also different from traditional free radical/high pressure polymerized LDPE. Surprisingly, the novel substantially linear ethylene polymers are also different from linear homogeneous ethylene polymers having a uniform comonomer distribution, especially with regard to processability.

These novel ethylene polymers, especially those with a density greater than or equal to 0.9 g/cm^3, are characterized as having:

a) a melt flow ratio, I_{10}/I_2, ≥ 5.63,

b) a molecular weight distribution, M_w/M_n, defined by the equation:
$M_w/M_n ≤ (I_{10}/I_2) - 4.63$,

c) a critical shear stress at onset of gross melt fracture greater than 4×10^6 dyne/cm^2, and

d) a single melt peak as determined by differential scanning calorimetry (DSC) between -30 and 150°C.

The novel ethylene polymers can also be characterized as having:

a) a melt flow ratio, I_{10}/I_2, ≥ 5.63,

b) a molecular weight distribution, M_w/M_n, defined by the equation:
$M_w/M_n ≤ (I_{10}/I_2) - 4.63$,

c) a critical shear rate at onset of surface melt fracture at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer with an I_2, M_w/M_n, and density each within ten percent of the novel ethylene polymer, and

d) a single melt peak as determined by differential scanning calorimetry (DSC) between -30 and 150°C.

In another aspect, the novel ethylene polymers, especially those having a density greater than or equal to about 0.9 g/cm^3, are characterized as having:

a) a melt flow ratio, I_{10}/I_2, ≥ 5.63, and

b) a molecular weight distribution, M_w/M_n of from 1.5 to 2.5,

c) a critical shear stress at onset of gross melt fracture greater than 4×10^6 dyne/cm^2, and

d) a single melt peak as determined by differential scanning calorimetry (DSC) between -30 and 150°C.

In still another aspect, the novel ethylene polymers are characterized as having:

a) a melt flow ratio, I_{10}/I_2, ≥ 5.63,

b) a molecular weight distribution, M_w/M_n of from 1.5 to 2.5,

c) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer with an I_2, M_w/M_n, and density each within ten percent of the novel ethylene polymer, and

d) a single melt peak as determined by differential scanning calorimetry (DSC) between -30 and 150°C.

The substantially linear ethylene polymers can also be characterized as having a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having an I_2, M_w/M_n and density each within ten percent of the substantially linear ethylene polymer.

In still another aspect the novel polymer can be characterized as a substantially linear ethylene bulk polymer having:

(a) an average of 0.01 to 3 long chain branches/1000 total carbons,

(b) a critical shear stress at onset of gross melt fracture of greater than 4×10^6 dyne/cm², and

(c) a single DSC melt peak between -30 and 150°C.

The substantially linear ethylene bulk polymer can also be characterized as having:

(a) an average of 0.01 to 3 long chain branches/1000 total carbons,

(b) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having an I_2, M_w/M_n and density each within ten percent of the substantially linear ethylene bulk polymer, and

(c) a single DSC melt peak between -30 and 150°C.

In still another aspect, the ethylene polymer can be characterized as a substantially linear ethylene bulk polymer having:

(a) an average of 0.01 to 3 long chain branches/1000 total carbons,

(b) a melt flow ratio, I_{10}/I_2, ≥ 5.63,

(c) a molecular weight distribution, M_w/M_n, from 1.5 to 2.5, and

(d) a single DSC melt peak between -30 and 150°C.

The novel ethylene polymers, especially the substantially linear ethylene polymers, also have a processing index (PI) less than or equal to 70 percent of the PI of a

-5-

linear ethylene polymer at about the same I_2, M_w/M_n, and density each within ten percent of the novel ethylene polymer.

Compositions comprising the novel ethylene polymer and at least one other natural or synthetic polymer are also within the scope of the invention.

Elastic substantially linear ethylene polymers comprising ethylene homopolymers or an interpolymer of ethylene with at least one C_3-C_{20} alpha-olefin copolymers are especially preferred.

Figure 1 is a schematic representation of a polymerization process suitable for making the polymers of the present invention.

Figure 2 plots data describing the relationship between I_{10}/I_2 and M_w/M_n for two examples of the invention, and for some comparative examples.

Figure 3 plots the shear stress versus shear rate for an Example of the invention and for a Comparative Example, described herein.

Figure 4 plots the shear stress versus shear rate for an Example of the invention and for a Comparative Example, described herein.

Figure 5 plots the heat seal strength versus heat seal temperature of film made from Examples of the invention, and for Comparative Examples, described herein.

Figure 6 graphically displays dynamic shear viscosity data for an elastic substantially linear ethylene polymer of the present invention and for a comparative linear polymer made using single site catalyst technology.

Figure 7 graphically displays I_{10}/I_2 ratio as a function of ethylene concentration in the polymerization reactor for ethylene/propene substantially linear copolymers of the invention.

Figure 8 graphically displays the melting curves for a comparative polymer made according to USP 5,218,071 (Mitsui).

Figure 9 graphically displays the structural characteristics of a traditional heterogeneous Ziegler polymerized LLDPE copolymers, a highly branched high pressure-free radical LDPE, and a novel substantially linear ethylene/alpha-olefin copolymer of the invention.

The term "linear" as used herein means that the ethylene polymer does not have long chain branching. That is, the polymer chains comprising the bulk linear ethylene polymer have an absence of long chain branching, as for example the traditional linear low density polyethylene polymers or linear high density polyethylene polymers made using Ziegler polymerization processes (for example, USP 4,076,698 (Anderson et al.)), sometimes called heterogeneous polymers. The term "linear" does not refer to bulk high pressure branched polyethylene, ethylene/vinyl acetate copolymers, or ethylene/vinyl alcohol copolymers which are known to those skilled in the art to have numerous long chain branches. The term "linear" also refers to polymers made using uniform branching distribution polymerization processes, sometimes called homogeneous polymers, including

-6-

narrow MWD (for example about 2) made using single site catalysts. Such uniformly branched or homogeneous polymers include those made as described in USP 3,645,992 (Elston) and those made using so-called single site catalysts in a batch reactor having relatively high ethylene concentrations (as described in U.S. Patent 5,026,798 (Canich) or

5   in U.S. Patent 5,055,438 (Canich)) or those made using constrained geometry catalysts in a batch reactor also having relatively high olefin concentrations (as described in U.S. Patent 5,064,802 (Stevens et al.) or in EP 0 416 815 A2 (Stevens et al.)). The uniformly branched/homogeneous polymers are those polymers in which the comonomer is randomly distributed within a given interpolymer molecule or chain, and wherein substantially all

10   of the interpolymer molecules have the same ethylene/comonomer ratio within that interpolymer, but these polymers too have an absence of long chain branching, as, for example, Exxon Chemical has taught in their February 1992 Tappi Journal paper. For example, Figure 9 shows the structural differences among conventional heterogeneously branched LLDPE, homogeneously branched linear LLDPE, highly branched high pressure,

15   free radical LDPE, and the homogeneously branched substantially linear ethylene polymers of the present invention.

The term "substantially linear" as used means that the bulk polymer is substituted, on average, with 0.01 long chain branches/1000 total carbons (including both backbone and branch carbons) to 3 long chain branches/1000 total carbons. Preferred polymers are

20   substituted with 0.01 long chain branches/1000 total carbons to 1 long chain branches/1000 total carbons, more preferably from 0.05 long chain branches/1000 total carbons to 1 long chain branched/1000 total carbons, and especially from 0.3 long chain branches/1000 total carbons to 1 long chain branches/1000 total carbons.

As used herein, the term "backbone" refers to a discrete molecule, and the term

25   "polymer" or "bulk polymer" refers in the conventional sense to the polmer as formed in a reactor. For the polymer to be a "substantially linear" polymer, the polymer must have at least enough molecules with long chain branching such that the average long chain branching in the bulk polymer is at least an average of 0.01/1000 total carbons.

The term "bulk" polymer means the polymer which results from the

30   polymerization process and, for the substantially linear polymers, includes molecules having both an absence of long chain branching, as well as molecules having long chain branching. Thus a "bulk" polymer includes all molecules formed during polymerization. It is understood that, for the substantially linear polymers, not all molecules have long chain branching, but a sufficient amount do such that the average long chain branching content of

35   the bulk polymer positively affects the melt rheology (that is, the melt fracture properties).

Long chain branching (LCB) is defined herein as a chain length of at least one (1) carbon less than the number of carbons in the comonomer, whereas short chain branching (SCB) is defined herein as a chain length of the same number of carbons in the residue of the

-7-

comonomer after it is incorporated into the polymer molecule backbone. For example, an ethylene/1-octene substantially linear polymer has backbones with long chain branches of at least seven (7) carbons in length, but it also has short chain branches of only six (6) carbons in length.

5   Long chain branching can be distinguished from short chain branching by using ^{13}C nuclear magnetic resonance (NMR) spectroscopy and to a limited extent, for example for ethylene homopolymers, it can be quantified using the method of Randall (Rev. Macromol.Chem. Phys., C29 (2&3), p. 285-297). However as a practical matter, current ^{13}C nuclear magnetic resonance spectroscopy cannot determine the length of a long chain branch

10   in excess of six (6) carbon atoms and as such, this analytical technique cannot distinguish between a seven (7) carbon branch and a seventy (70) carbon branch. The long chain branch can be as long as about the same length as the length of the polymer back-bone.

USP 4,500,648 teaches that long chain branching frequeny (LCB) can be represented by the equation $LCB=b/M_w$ wherein b is the weight average number of long chain branches

15   per molecule and M_w is the weight average molecular weight. The molecular weight averages and the long chain branching characteristics are determined by gel permeation chromatography and intrinsic viscosity methods.

Similar to the traditional homogeneous polymers, the substantially linear ethylene/alpha-olefin copolymers of the invention have only a single melting point, as

20   opposed to traditional Ziegler polymerized heterogeneous linear ethylene/alpha-olefin copolymers which have two or more melting points (determined using differential scanning calorimetry (DSC)). Ethylene polymers of this invention are also characterized by a single DSC melting peak between -30 and 150°C. However, those polymers having a density of 0.875 g/cm^3 to 0.91 g/cm^3, the single melt peak may show, depending on equipment

25   sensitivity, a "shoulder" or a "hump" on the low side of the melting peak (that is below the melting point) that constitutes less than 12 percent, typically, less than 9 percent, more typically less than 6 percent of the total heat of fusion of the polymer. This artifact is due to intrapolymer chain variations, and it is discerned on the basis of the slope of the single melting peak varying monotonically through the melting region of the artifact. Such

30   artifact occurs within 34°C, typically within 27°C, and more typically within 20°C of the melting point of the single melting peak. The single melting peak is determined using a differential scanning calorimeter standardized with indium and deionized water. The method involves about 5-7 mg sample sizes, a "first heat" to about 150°C which is held for 4 minutes, a cool down at 10°C/min. to -30°C which is held for 3 minutes, and heat up at

35   10°C/min. to 150°C for the "second heat" heat flow vs. temperature curve. Total heat of fusion of the polymer is calculated from the area under the curve. The heat of fusion attributable to this artifact, if present, can be determined using an analytical balance and weight-percent calculations.

Figure 8 displays the melting curves for a polymer of the invention and for a comparative polymer as described in USP 5,218,071 (Mitsui). Note that the comparative polymer has two melting peaks (the high melting peak with a shoulder on its high side, that is above the second melting point), and this is indicative of the presence of two

5   distinct polymers (as opposed to the melting curve of the invention polymer having only a single melting peak).

The SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content.

10   The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, in Wild et al, Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982), or as described in U.S. Patent 4,798,081. The SCBDI or CDBI for the substantially linear ethylene polymers of the present invention is typically greater

15   than 30 percent, preferably greater than 50 percent, more preferably greater than 80 percent, and most preferably greater than 90 percent.

"Melt tension" is measured by a specially designed pulley transducer in conjunction with the melt indexer. Melt tension is the load that the extrudate or filament exerts while passing over the pulley onto a two inch drum that is rotating at the standard speed of 30

20   rpm. The melt tension measurement is similar to the "Melt Tension Tester" made by Toyoseiki and is described by John Dealy in "Rheometers for Molten Plastics", published by Van Nostrand Reinhold Co. (1982) on page 250-251. The melt tension of these new polymers is also surprisingly good, for example, as high as 2 grams or more. For the novel substantially linear ethylene interpolymers of this invention, especially those having a

25   very narrow molecular weight distribution (that is, M_w/M_n from 1.5 to 2.5), the melt tension is typically at least 5 percent, and can be as much as 60 percent, greater than the melt tension of a conventional linear ethylene interpolymer having a melt index, polydispersity and density each within ten percent of the substantially linear ethylene polymer.

30   A unique characteristic of the presently claimed polymers is a highly unexpected flow property where the I_{10}/I_2 value is essentially independent of polydispersity index (that is M_w/M_n). This is contrasted with conventional Ziegler polymerized heterogeneous polyethylene resins and with conventional single site catalyst polymerized homogeneous polyethylene resins having rheological properties such that as the polydispersity index

35   increases, the I_{10}/I_2 value also increases.

The density of the neat ethylene or substantially linear ethylene polymers of this invention, that is polymers without inorganic fillers and not containing in excess of 20 ppm aluminum from catalyst residue, is measured in accordance with ASTM D-792. The ethylene or substantially linear ethylene polymers are crystalline and/or semi-crystalline

-9-

polymers, are normally solid at room temperature, and are pelletizable at ambient conditions or at temperatures induced by cooled water. For example, a novel substantially linear ethylene/1-octene copolymer having a density of 0.865 g/cm^3 has about 10 percent crystallinity at room temperature. The minimum density is typically at least 0.865 g/cm^3, preferably at least 0.870 g/cm^3, and more preferably at least 0.900 g/cm^3. The maximum density typically does not exceed 0.970 g/cm^3, preferably it does not exceed 0.940 g/cm^3, and more preferably it does not exceed 0.92 g/cm^3.

The molecular weight of the ethylene or ethylene/alpha-olefin substantially linear ethylene polymers in the present invention is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190 C/2.16 kg (formally known as "Condition (E)" and also known as I_2). Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. The melt index for the ethylene or ethylene/alpha-olefin substantially linear ethylene polymers used herein is generally from 0.01 grams/10 minutes (g/10 min) to 1000 g/10 min, preferably from 0.01 g/10 min to 100 g/10 min, and especially from 0.01 g/10 min to 10 g/10 min.

Another measurement useful in characterizing the molecular weight of the substantially linear ethylene polymers is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190C/10 kg (formerly known as "Condition (N)" and also known as I_{10}). The ratio of these two melt index terms is the melt flow ratio and is designated as I_{10}/I_2. For the substantially linear ethylene/alpha-olefin polymers of the invention, the I_{10}/I_2 ratio indicates the degree of long chain branching, that is, the higher the I_{10}/I_2 ratio, the more long chain branching in the polymer. Generally, the I_{10}/I_2 ratio of the substantially linear ethylene/alpha-olefin polymers is at least 5.63, preferably at least 7, especially at least 8, most especially at least 9 or above. The only limitations on the maximum I_{10}/I_2 ratio are practical considerations such as economics, polymerization kinetics, etc., but typically the maximum I_{10}/I_2 ratio does not exceed 20, and preferably it does not exceed 15.

Antioxidants (for example, hindered phenolics (for example, Irganox® 1010 made by Ciba Geigy Corp.), phosphites (for example, Irgafos® 168 made by Ciba Geigy Corp.)), are preferably added to protect the polymer from degradation during thermal processing steps such as pelletization, molding, extrusion, and characterization methods. Other additives to serve special functional needs include cling additives, for example PIB, antiblocks, antislips, pigments, and fillers. In-process additives, for example calcium stearate, water, etc., may also be used for other purposes such as for the deactivation of residual catalyst. However, peroxide need not be added to the novel polymers in order for the polymers to exhibit an I_{10}/I_2 independent of the MWD and the melt fracture properties.

Molecular Weight Distribution Determination

        The whole interpolymer product samples and the individual interpolymer samples
are analyzed by gel permeation chromatography (GPC) on a Waters 150 C high
temperature chromatographic unit equipped with three linear mixed porosity bed columns
(available from Polymer Laboratories), operating at a system temperature of 140°C. The
solvent is 1,2,4-trichlorobenzene, from which 0.3 percent by weight solutions of the samples
are prepared for injection. The flow rate is 1.0 milliliters/minute and the injection size is
200 microliters.

        The molecular weight determination is deduced by using narrow molecular weight
distribution polystyrene standards (from Polymer Laboratories) in conjunction with their
elution volumes. The equivalent polyethylene molecular weights are determined by using
appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by
Williams and Ward in Journal of Polymer Science, Polymer Letters, Vol. 6, (621) 1968) to
derive the following equation:

$$M_{polyethylene} = a * (M_{polystyrene})^b.$$

In this equation, a = 0.4316 and b = 1.0 for polyethylene and polystyrene in 1,2,4-
trichlorobenzene. Weight average molecular weight, M_w, is calculated in the usual
manner according to the following formula: $M_w = \Sigma w_i * M_i$, where w_i and M_i are the
weight fraction and molecular weight, respectively, of the ith fraction eluting from the
GPC column.

        The molecular weight distribution (M_w/M_n) for the substantially linear ethylene
polymers of the invention is generally less than 5, preferably from 1.5 to 2.5, and especially
from 1.7 to 2.3.

Processing Index Determination

        The "rheological processing index" (PI) is the apparent viscosity (in kpoise) of a
polymer and is measured by a gas extrusion rheometer (GER). The GER is described by M.
Shida, R.N. Shroff and L.V. Cancio in Polym. Eng. Sci., Vol. 17, no. 11, p. 770 (1977), and in
"Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co.
(1982) on page 97-99. The processing index is measured at a temperature of 190°C, at
nitrogen pressure of 17.3 MPa (2500 psig) using a 752 micrometers (0.0296 inch) diameter
(preferably 363 micrometers (0.0143 inch) diameter die for high flow polymers, for example
50 - 100 melt index or greater), 20:1 L/D die having an entrance angle of 180 degrees. The
GER processing index is calculated in millipoise units from the following equation:
        PI = 2.15 X 10^6 dyne/cm^2/(1000 X shear rate),

-11-

where: 2.15 X 10^6 dyne/cm^2 is the shear stress (at 2500 psig), and the shear rate is the shear rate at the wall as represented by the following equation:

32 Q'/ (60 sec/min)(0.745)(Diameter X 2.54 cm/in)^3, where:

Q' is the extrusion rate (gms/min),

0.745 is the melt density of polyethylene (gm/cm^3), and

Diameter is the orifice diameter of the capillary (inches).

The PI is the apparent viscosity of a material measured at apparent shear stress of 2.15 x 10^6 dyne/cm^2.

For the substantially linear ethylene polymers (or ethylene/alpha-olefin copolymers or interpolymers), the PI is less than or equal to 70 percent of that of a conventional linear ethylene polymer (or ethylene/alpha-olefin copolymer or interpolymer) having an I_2, M_w/M_n and density each within ten percent of the substantially linear ethylene polymer.

An apparent shear stress vs. apparent shear rate plot is used to identify the melt fracture phenomena over a range of nitrogen pressures from 36.3 MPa to 3.55 MPa (5250 to 500 psig) using the die or GER test apparatus previously described. According to Ramamurthy in Journal of Rheology, 30(2), 337-357, 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular gloss to the more severe form of "sharkskin". In this disclosure, the onset of surface melt fracture is characterized at the beginning of losing extrudate gloss at which the surface roughness of extrudate can only be detected by 40X magnification. The critical shear rate at onset of surface melt fracture for the substantially linear ethylene polymers is at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having about the same I_2 and M_w/M_n. Preferably, the critical shear stress at onset of surface melt fracture for the substantially linear ethylene polymers of the invention is greater than 2.8 x 10^6 dyne/cm^2.

Gross melt fracture occurs at unsteady flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (for example, in blown film products), surface defects should be minimal, if not absent. The critical shear rate at onset of surface melt fracture (OSMF) and critical shear stress at onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER. For the substantially linear ethylene polymers of the invention, the critical shear stress at onset of gross melt fracture is preferably greater than 4 x 10^6 dyne/cm^2.

For the processing index deterination and for the GER melt fracture determination, the novel ethylene or substantially linear ethylene copolymers are tested without inorganic fillers, and they do not have more than 20 ppm aluminum catalyst residue.
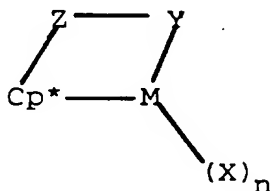
-12-

Preferably, however, for the processing index and melt fracture tests, the novel ethylene polymers and substantially linear ethylene copolymers do contain antioxidants such as phenols, hindered phenols, phosphites or phosphonites, preferably a combination of a phenol or hindered phenol and a phosphite or a phosphonite.

The Constrained Geometry Catalyst

Suitable constrained geometry catalysts for use herein preferably include constrained geometry catalysts as disclosed in U.S. Application Serial Nos.: 545,403, filed July 3, 1990; 758,654, filed September 12, 1991; 758,660, filed September 12, 1991; and 720,041, filed June 24, 1991. The monocyclopentadienyl transition metal olefin polymerization catalysts taught in USP 5,026,798 are also believed to be suitable for use in preparing the polymers of the present invention, so long as the polymerization conditions substantially conform to those described herein.

The foregoing catalysts may be further described as comprising a metal coordination complex comprising a metal of groups 3-10 or the Lanthanide series of the Periodic Table of the Elements and a delocalized π-bonded moiety substituted with a constrain-inducing moiety, said complex having a constrained geometry about the metal atom such that the angle at the metal between the centroid of the delocalized, substituted π-bonded moiety and the center of at least one remaining substituent is less than such angle in a similar complex containing a similar π-bonded moiety lacking in such constrain-inducing substituent, and provided further that for such complexes comprising more than one delocalized, substituted π-bonded moiety, only one thereof for each metal atom of the complex is a cyclic, delocalized, substituted π-bonded moiety. The catalyst further comprises an activating cocatalyst.

Preferred catalyst complexes correspond to the formula:

$$\begin{array}{c} Z \!-\!\!-\!\!- Y \\ \diagup \quad \quad \diagup \\ Cp^* \!-\!\!-\!\!- M \\ \diagdown \\ (X)_n \end{array}$$

-13-

wherein:

M is a metal of group 3-10, or the Lanthanide series of the Periodic Table of
the Elements;

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5
bonding mode to M;

Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the
Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms,
and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group or neutral Lewis base
ligand group having up to 30 non-hydrogen atoms;

n is 0, 1, 2, 3, or 4 and is 2 less than the valence of M; and

Y is an anionic or nonanionic ligand group bonded to Z and M comprising nitrogen,
phosphorus, oxygen or sulfur and having up to 20 non-hydrogen atoms, optionally Y and Z
together form a fused ring system.

More preferably still, such complexes correspond to the formula:
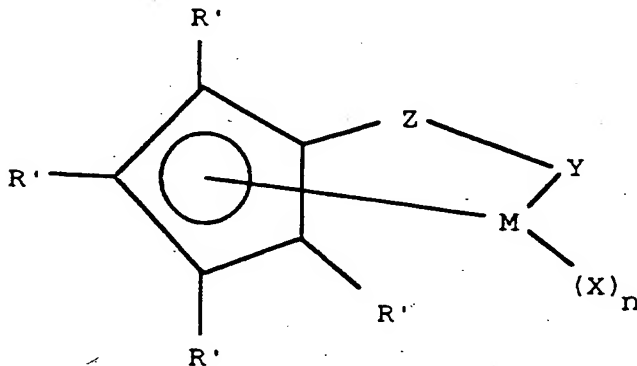
wherein:

R' each occurrence is independently selected from the group consisting of hydrogen,
alkyl, aryl, silyl, germyl, cyano, halo and combinations thereof having up to 20
non-hydrogen atoms;

X each occurrence independently is selected from the group consisting of hydride,
halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, neutral Lewis base ligands
and combinations thereof having up to 20 non-hydrogen atoms;

Y is -O-, -S-, -NR*-, -PR*-, or a neutral two electron donor ligand selected from the
group consisting of OR*, SR*, NR*$_2$ or PR*$_2$;

-14-

M is as previously defined; and

Z is SiR^*_2, CR^*_2, $SiR^*_2SiR^*_2$, $CR^*_2CR^*_2$, $CR^*=CR^*$, $CR^*_2SiR^*_2$, GeR^*_2, BR^*, BR^*_2; wherein

R* each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups having up to 20 non-hydrogen atoms, and mixtures thereof, or two or more R* groups from Y, Z, or both Y and Z form a fused ring system; and n is 1 or 2.

It should be noted that whereas formula I and the following formulas indicate a cyclic structure for the catalysts, when Y is a neutral two electron donor ligand, the bond between M and Y is more accurately referred to as a coordinate-covalent bond. Also, it should be noted that the complex may exist as a dimer or higher oligomer.

Further preferably, at least one of R', Z, or R* is an electron donating moiety. Thus, highly preferably Y is a nitrogen or phosphorus containing group corresponding to the formula -N(R")- or -P(R")-, wherein R" is C_{1-10} alkyl or aryl, that is, an amido or phosphido group.

Most highly preferred complex compounds are amidosilane- or amidoalkanediyl- compounds corresponding to the formula:
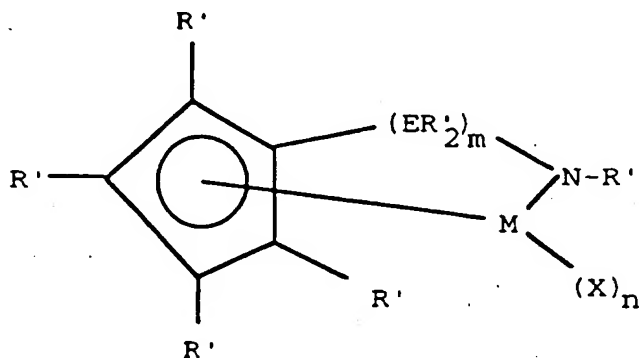
wherein:

M is titanium, zirconium or hafnium, bound in an η^5 bonding mode to the cyclopentadienyl group;

R' each occurrence is independently selected from the group consisting of hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms;

E is silicon or carbon;

X independently each occurrence is hydride, halo, alkyl, aryl, aryloxy or alkoxy of up to 10 carbons;

m is 1 or 2; and

n is 1 or 2.

-15-

Examples of the above most highly preferred metal coordination compounds include compounds wherein the R' on the amido group is methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; the cyclopentadienyl group is

5   cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl, etc.; R' on the foregoing cyclopentadienyl groups each occurrence is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; and X is chloro, bromo, iodo, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc. Specific compounds include: (tert-butylamido)(tetramethyl-

10 η^5-cyclopentadienyl)-1,2-ethanediylzirconium dichloride,
(tert-butylamido)(tetramethyl- η^5-cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (methylamido)(tetramethyl- η^5-cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (methylamido)(tetramethyl- η^5-cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (ethylamido)(tetramethyl- η^5-cyclopentadienyl)-methylenetitanium

15 dichloro, (tertbutylamido)dibenzyl(tetramethyl- η^5-cyclopentadienyl) silanezirconium dibenzyl, (benzylamido)dimethyl- (tetramethyl- η^5-cyclopentadienyl)silanetitanium dichloride, (phenylphosphido)dimethyl(tetramethyl- η^5-cyclopentadienyl)silanezirconium dibenzyl, and
(tertbutylamido)dimethyl(tetramethyl- η^5-cyclopentadienyl)silanetitanium dimethyl.

20   The complexes may be prepared by contacting a derivative of a metal, M, and a group I metal derivative or Grignard derivative of the cyclopentadienyl compound in a solvent and separating the salt byproduct. Suitable solvents for use in preparing the metal complexes are aliphatic or aromatic liquids such as cyclohexane, methylcyclohexane, pentane, hexane, heptane, tetrahydrofuran, diethyl ether, benzene, toluene, xylene,

25 ethylbenzene, etc., or mixtures thereof.

In a preferred embodiment, the metal compound is MX_{n+1}, that is, M is in a lower oxidation state than in the corresponding compound, MX_{n+2} and the oxidation state of M in the desired final complex. A noninterfering oxidizing agent may thereafter be employed to raise the oxidation state of the metal. The oxidation is accomplished merely by contacting

30 the reactants utilizing solvents and reaction conditions used in the preparation of the complex itself. By the term "noninterfering oxidizing agent" is meant a compound having an oxidation potential sufficient to raise the metal oxidation state without interfering with the desired complex formation or subsequent polymerization processes. A particularly suitable noninterfering oxidizing agent is AgCl or an organic halide such as methylene

35 chloride. The foregoing techniques are disclosed in U.S. Ser. Nos.: 545,403, filed July 3, 1990 and 702,475, filed May 20, 1991.

Additionally the complexes may be prepared according to the teachings of the copending United States application serial number 778,433 entitled: "Preparation of Metal Coordination Complex (I)", filed in the names of Peter Nickias and David Wilson, on

-16-

October 15, 1991 and the copending United States application serial number 778,432 entitled: "Preparation of Metal Coordination Complex (II)", filed in the names of Peter Nickias and David Devore, on October 15, 1991, and the patents issuing therefrom.

Suitable cocatalysts for use herein include polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. So called modified methyl aluminoxane (MMAO) is also suitable for use as a cocatalyst. One technique for preparing such modified aluminoxane is disclosed in USP 5,041,584. Aluminoxanes can also be made as disclosed in USP 5,218,071; 5,086,024, 5,041,585, 5,041,583, 5,015,749, 4,960,878 and 4,544,762. Aluminoxanes, including modified methyl aluminoxanes, when used in the polymerization, are preferably used such that preferably less than about 20 ppm aluminum, especially less than about 10 ppm aluminum, and more preferably less than about 5 ppm aluminum, from catalyst residue remain in the polymer. In order to measure the bulk polymer properties (for example PI or melt fracture), aqueous HCl is used to extract the aluminoxane from the polymer. Preferred cocatalysts, however, are inert, noncoordinating, boron compounds such as those described in EP 520732.

Ionic active catalyst species which can be used to polymerize the polymers described herein correspond to the formula:
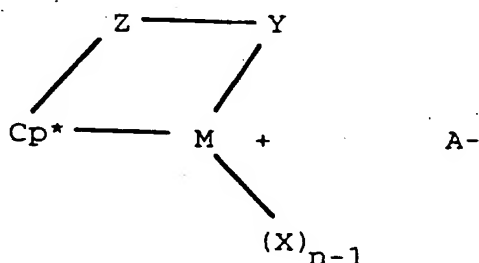
$$
\begin{array}{ccc}
 & Z \rule[0.5ex]{2em}{0.4pt} Y & \\
\diagup & \diagup & \\
Cp^* \rule[0.5ex]{2em}{0.4pt} M \;\; + & & A- \\
 & \diagdown & \\
 & (X)_{n-1} &
\end{array}
$$

wherein:

M is a metal of group 3-10, or the Lanthanide series of the Periodic Table of the Elements;

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M;

Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group or neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

n is 0, 1, 2, 3, or 4 and is 2 less than the valence of M; and

A- is a noncoordinating, compatible anion.

-17-

One method of making the ionic catalyst species which can be utilized to make the polymers of the present invention involve combining:

a) at least one first component which is a mono(cyclopentadienyl) derivative of a metal of Group 3-10 or the Lanthanide Series of the Periodic Table of the Elements containing at least one substituent which will combine with the cation of a second component (described hereinafter) which first component is capable of forming a cation formally having a coordination number that is one less than its valence, and

b) at least one second component which is a salt of a Bronsted acid and a noncoordinating, compatible anion.

More particularly, the non-coordinating, compatible anion of the Bronsted acid salt may comprise a single coordination complex comprising a charge-bearing metal or metalloid core, which anion is both bulky and non-nucleophilic. The recitation "metalloid", as used herein, includes non-metals such as boron and phosphorus which exhibit semi-metallic characteristics.

Illustrative, but not limiting examples of monocyclopentadienyl metal components (first components) which may be used in the preparation of cationic complexes are derivatives of titanium, zirconium, vanadium, hafnium, chromium, lanthanum, etc. Preferred components are titanium or zirconium compounds. Examples of suitable monocyclopentadienyl metal compounds are hydrocarbyl-substituted monocyclopentadienyl metal compounds such as (tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediylzirconium dimethyl, (tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyltitanium dimethyl, (methylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediylzirconium dibenzyl,

(methylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyltitanium dimethyl, (ethylamido)(tetramethyl-η^5-cyclopentadienyl)methylenetitanium dimethyl, (tertbutylamido)dibenzyl(tetramethyl-η^5-cyclopentadienyl) silanezirconium dibenzyl, (benzylamido)dimethyl-

(tetramethyl-η^5-cyclopentadienyl)silanetitanium diphenyl,

(phenylphosphido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silanezirconium dibenzyl.

Such components are readily prepared by combining the corresponding metal chloride with a dilithium salt of the substituted cyclopentadienyl group such as a cyclopentadienyl-alkanediyl, cyclopentadienyl-silane amide, or cyclopentadienyl-phosphide compound. The reaction is conducted in an inert liquid such as tetrahydrofuran, C_{5-10} alkanes, toluene, etc. utilizing conventional synthetic procedures. Additionally, the first components may be prepared by reaction of a group II derivative of the cyclopentadienyl compound in a solvent and separating the salt by-product. Magnesium derivatives of the cyclopentadienyl compounds are preferred. The reaction may be conducted in an inert solvent such as cyclohexane, pentane, tetrahydrofuran, diethyl ether,

-18-

benzene, toluene, or mixtures of the like. The resulting metal cyclopentadienyl halide complexes may be alkylated using a variety of techniques. Generally, the metal cyclopentadienyl alkyl or aryl complexes may be prepared by alkylation of the metal cyclopentadienyl halide complexes with alkyl or aryl derivatives of group I or group II

5. metals. Preferred alkylating agents are alkyl lithium and Grignard derivatives using conventional synthetic techniques. The reaction may be conducted in an inert solvent such as cyclohexane, pentane, tetrahydrofuran, diethyl ether, benzene, toluene, or mixtures of the like. A preferred solvent is a mixture of toluene and tetrahydrofuran.

Compounds useful as a second component in the preparation of the ionic catalysts

10 useful in this invention will comprise a cation, which is a Bronsted acid capable of donating a proton, and a compatible noncoordinating anion. Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 3-10 or Lanthanide Series cation) which is formed when the two components are

15 combined and sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases such as ethers, nitriles and the like. Suitable metals, then, include, but are not limited to, aluminum, gold, platinum and the like. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon and the like. Compounds containing anions which comprise coordination complexes containing a

20 single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially. In light of this, salts containing anions comprising a coordination complex containing a single boron atom are preferred.

Highly preferably, the second component useful in the preparation of the catalysts

25 of this invention may be represented by the following general formula:

$$(L-H)+ \ [A]-$$
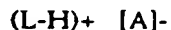
wherein:

L is a neutral Lewis base;

(L-H)+ is a Bronsted acid; and

30 [A]⁻ is a compatible, noncoordinating anion.

More preferably [A]⁻ corresponds to the formula:

$$[M'Q_q]^-$$

35 wherein:

M' is a metal or metalloid selected from Groups 5-15 of the Periodic Table of the Elements; and

-19-

Q independently each occurrence is selected from the Group consisting of hydride, dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, and halo substituted-hydrocarbyl radicals of up to 20 carbons with the proviso that in not more than one occurrence is Q halide and

5   q is one more than the valence of M'.

Second components comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:

10

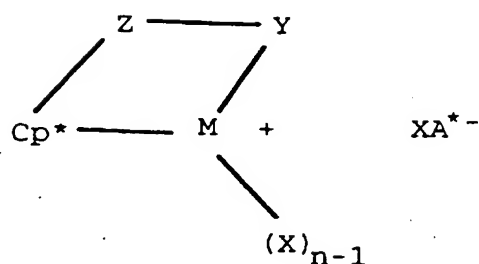$$[L-H]^+ [BQ_4]^-$$
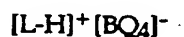
wherein:

L is a neutral Lewis base;

15          $[L-H]^+$ is a Bronsted acid;

B is boron in a valence state of 3; and

Q is as previously defined.

Illustrative, but not limiting, examples of boron compounds which may be used as a

20 second component in the preparation of the improved catalysts of this invention are trialkyl-substituted ammonium salts such as triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tris(n-butyl)ammonium tetraphenylborate, trimethylammonium tetrakis(p-tolyl)borate, tributylammonium tetrakis(pentafluorophenyl)borate, tripropylammonium tetrakis(2,4-

25 dimethylphenyl)borate, tributylammonium tetrakis(3,5-dimethylphenyl)borate, triethylammonium tetrakis(3,5-di-trifluoromethylphenyl)borate and the like. Also suitable are N,N-dialkyl anilinium salts such as N,N-dimethyl-aniliniumtetraphenylborate, N,N-diethylanilinium tetraphenylborate, N,N-2,4,6-pentamethylanilinium tetraphenylborate and the like; dialkylammonium salts such as di-

30 (i-propyl)ammonium tetrakis(pentafluorophenyl)borate, dicyclohexylammonium tetraphenylborate and the like; and triaryl phosphonium salts such as triphenylphosphonium tetraphenylborate, tri(methylphenyl)phosphonium tetrakis-pentafluorophenylborate, tri(dimethylphenyl)phosphonium tetraphenylborate and the like.

35   Preferred ionic catalysts are those having a limiting charge separated structure corresponding to the formula:

-20-

$$Cp^* \xrightarrow{\qquad} \overset{\displaystyle Z \xrightarrow{\qquad} Y}{M} \quad + \quad XA^{*-}$$
$$(X)_{n-1}$$

wherein:

M is a metal of group 3-10, or the Lanthanide series of the Periodic Table of the Elements;

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M;

Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group or neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

n is 0, 1, 2, 3, or 4 and is 2 less than the valence of M; and

XA^{*-} is $-XB(C_6F_5)_3$.

This class of cationic complexes may be conveniently prepared by contacting a metal compound corresponding to the formula:

$$Cp^* \xrightarrow{\qquad} \overset{\displaystyle Z \xrightarrow{\qquad} Y}{M}$$
$$(X)_n$$
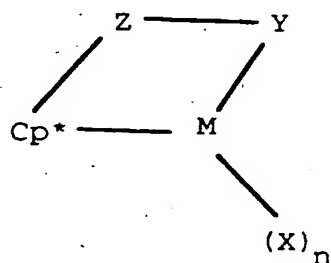
wherein:

Cp*, M, and n are as previously defined,

with tris(pentafluorophenyl)borane cocatalyst under conditions to cause abstraction of X and formation of the anion $-XB(C_6F_5)_3$.

Preferably X in the foregoing ionic catalyst is C_1-C_{10} hydrocarbyl, most preferably methyl.

-21-

The preceding formula is referred to as the limiting, charge separated structure. However, it is to be understood that, particularly in solid form, the catalyst may not be fully charge separated. That is, the X group may retain a partial covalent bond to the metal atom, M. Thus, the catalysts may be alternately depicted as possessing the formula:
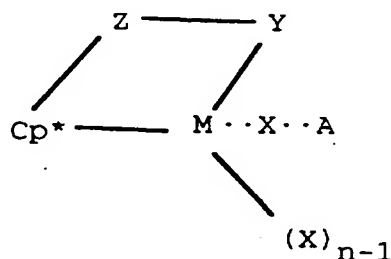
$$
\begin{array}{c}
Z \text{------} Y \\
\diagup \quad\quad \diagup \\
Cp^* \text{------} M \cdots X \cdots A \\
\diagdown \\
(X)_{n-1}
\end{array}
$$

The catalysts are preferably prepared by contacting the derivative of a Group 4 or Lanthanide metal with the tris(pentafluorophenyl)borane in an inert diluent such as an organic liquid. Tris(pentafluorophenyl)borane is a commonly available Lewis acid that may be readily prepared according to known techniques. The compound is disclosed in Marks, et al. J. Am. Chem. Soc. 1991, 113, 3623-3625 for use in alkyl abstraction of zirconocenes.

All reference to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1989. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

It is believed that in the constrained geometry catalysts used herein the metal atom is forced to greater exposure of the active metal site because one or more substituents on the single cyclopentadienyl or substituted metal is both bonded to an adjacent covalent moiety and held in association with the cyclopentadienyl group through an η^5 or other π-bonding interaction. It is understood that each respective bond between the metal atom and the constituent atoms of the cyclopentadienyl or substituted cyclopentadienyl group need not be equivalent. That is, the metal may be symmetrically or unsymmetrically π-bound to the cyclopentadienyl or substituted cyclopentadienyl group.

The geometry of the active metal site is further defined as follows. The centroid of the cyclopentadienyl or substituted cyclopentadienyl group may be defined as the average of the respective X, Y, and Z coordinates of the atomic centers forming the cyclopentadienyl or substituted cyclopentadienyl group. The angle, Θ, formed at the metal center between the centroid of the cyclopentadienyl or substituted cyclopentadienyl group and each other ligand of the metal complex may be easily calculated by standard techniques of single

crystal X-ray diffraction. Each of these angles may increase or decrease depending on the molecular structure of the constrained geometry metal complex. Those complexes wherein one or more of the angles, Θ, is less than in a similar, comparative complex differing only in the fact that the constrain inducing substituent is replaced by hydrogen, have constrained geometry for purposes of the present invention. Preferably one or more of the above angles, Θ, decrease by at least 5 percent, more preferably 7.5 percent, compared to the comparative complex. Highly preferably, the average value of all bond angles, Θ, is also less than in the comparative complex.

Preferably, monocyclopentadienyl metal coordination complexes of group 4 or lanthanide metals according to the present invention have constrained geometry such that the smallest angle, Θ, between the centroid of the Cp* group and the Y substituent, is less than 115 degrees, more preferably less than 110 degrees, most preferably less than 105 degrees, and especially less than 100 degrees.
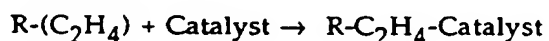
Other compounds which are useful in the catalyst compositions of this invention, especially compounds containing other Group 4 or Lanthanide metals, will, of course, be apparent to those skilled in the art.

Polymerization

The improved melt elasticity and processibility of the substantially linear polymers according to the present invention result, it is believed, from their method of production. The polymers may be produced via a continuous (as opposed to a batch) controlled polymerization process using at least one reactor (for example, as disclosed in WO 93/07187, WO 93/07188, and WO 93/07189), but can also be produced using multiple reactors (for example, using a multiple reactor configuration as described in USP 3,914,342) at a polymerization temperature and pressure sufficient to produce the interpolymers having the desired properties.

While not wishing to be bound by any particular theory, the inventors believe that long chain branches are formed in their novel polymers according to the following sequence:

Propagation Step

$$R\text{-}(C_2H_4) + \text{Catalyst} \rightarrow R\text{-}C_2H_4\text{-Catalyst}$$

Termination Step

$$R\text{-}C_2H_4\text{-Catalyst} \rightarrow R\text{-}CH=CH_2 \text{ (beta-hydride elimination)}$$

Copolymerization

$$R\text{-}CH_2\text{-}CH_2\text{-}CHR'\text{-}CH_2\text{-Catalyst} \rightarrow$$
$$R\text{-}CH_2\text{-}CH_2\text{-}CHR'\text{-}CH_2\text{-Catalyst}$$

-23-
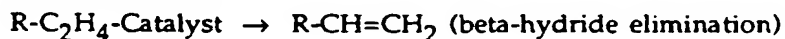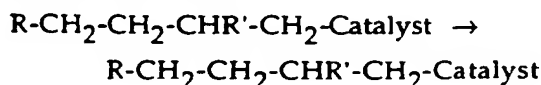
Continued Polymerization

R-CH$_2$-CH$_2$-CHR'-CH$_2$-Catalyst + (C$_2$H$_4$)$_x$ →

     R-CHR'(CH$_2$CH$_2$)$_x$-Catalyst

Termination Step

1)   R-CHR'(CH$_2$CH$_2$)$_x$-Catalyst + Heat →

     R-CHR'R"CH=CH$_2$ + H-Catalyst

2)   R-CHR'(CH$_2$CH$_2$)$_x$-Catalyst + H$_2$ →

     R-CHR'R" + H-Catalyst
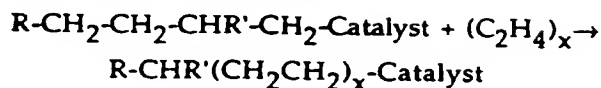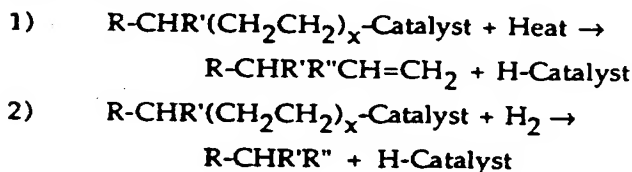
wherein: R = growing polymer chain

     R'= long chain branch (LCB), and

     R"= growing polymer chain after insertion of R".

In polymerizing ethylene and ethylene/alpha-olefin copolymers, a batch reactor process typically operates at an ethylene concentration from 6.7 to 12.5 percent by weight of the reactor contents and have a polymer concentration generally less than 5 percent by weight of the reactor contents, dependent upon the ethylene solubility, which is a function of reactor diluent, temperature and pressure. The inititial polymer concentration is zero and increases over time as the reaction proceeds such that the highest polymer concentration occurs at the end of the reaction, the point at which the catalyst is spent. Most of the polymer is made during the initial minutes of the polymerization.

According to one embodiment of the present process, the polymers are produced in a continuous process operated at a steady state (that is the reactants are fed to the reactor at a rate in substantially in balance with the rate that product is removed from the reactor such that the reaction mass in the reactor is relatively constant in volume and composition), as opposed to a batch process. Preferably, the polymerization temperature of the continuous process is from about 20 C to about 250 C, using constrained geometry catalyst technology. If a narrow molecular weight distribution polymer (M_w/M_n of from 1.5 to 2.5) having a higher I_{10}/I_2 ratio (for example I_{10}/I_2 of 7 or more, preferably at least 8, especially at least 9 and as high as 20 or more) is desired, the ethylene concentration in the reactor is preferably not more than 8 percent by weight of the reactor contents, especially not more than 6 percent by weight of the reactor contents, and most especially not more than 4 percent by weight of the reactor contents, and as low as 0.75 percent by weight of the reactor contents. Preferably, the polymerization is performed in a solution polymerization process. Generally, manipulation of I_{10}/I_2 while holding M_w/M_n relatively low for producing the novel polymers described herein is a function of reactor temperature and/or ethylene concentration. Surprisingly, reduced ethylene concentration and higher temperature generally produces higher I_{10}/I_2. Generally, as the percent of ethylene is

-24-

converted into polymer, the ethylene concentration in the reactor decreases and the polymer concentration increases. For the novel substantially linear ethylene/alpha-olefin copolymers and substantially linear ethylene homopolymers claimed herein, the polymer concentration for a continuous solution polymerization process is preferably above 5 weight

5   percent of the reactor contents, especially above 15 weight percent of the reactor contents, and as high as 40 weight percent of the reactor contents. Typically greater than 70 percent, preferably greater than 80 percent and more preferably greater than 90 percent, of the ethylene is converted to polymer.

The substantially linear polymers of the present invention can be ethylene

10 homopolymers, or they can be interpolymers of ethylene with at least one C_3-C_{20} alpha-olefin and/or C_4-C_{18} diolefins. The substantially linear polymers of the present invention can also be interpolymers of ethylene with at least one of the above C_3-C_{20} alpha-olefins and/or diolefins in combination with other unsaturated monomers.

Monomers usefully copolymerized or interpolymerized with ethylene according to

15 the present invention include, for example, ethylenically unsaturated monomers, conjugated or nonconjugated dienes, polyenes, etc. Preferred comonomers include the C_3-C_{10} alpha-olefins especially propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene, halo- or alkyl substituted styrenes, vinylbenzocyclobutene, 1,4-hexadiene, and naphthenics (for example, cyclo-pentene,

20 cyclo-hexene and cyclo-octene).

Other unsaturated monomers usefully copolymerized according to the present invention include, for example, ethylenically unsaturated monomers, conjugated or nonconjugated dienes, polyenes, etc. Preferred comonomers include the C_3-C_{10} alpha-olefins especially propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene,

25 and 1-octene. Other preferred comonomers include styrene, halo- or alkyl substituted styrenes, vinylbenzocyclobutene, 1,4-hexadiene, and naphthenics (for example, cyclopentene, cyclohexene and cyclooctene).

The polymerization conditions for manufacturing the polymers of the present invention are generally those useful in the solution polymerization process, although the

30 application of the present invention is not limited thereto. Slurry and gas phase polymerization processes are also believed to be useful, provided the proper catalysts and polymerization conditions are employed.

Multiple reactor polymerization processes are also useful in the present invention, such as those disclosed in USP 3,914,342. The multiple reactors can be operated in series or

35 in parallel, with at least one constrained geometry catalyst employed in at least one of the reactors.

In general, the continuous polymerization according to the present invention may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0 to 250°C and

-25-

pressures from atmospheric to 1000 atmospheres (100 MPa). Suspension, solution, slurry, gas phase or other process conditions may be employed if desired. A support may be employed, but preferably the catalysts are used in a homogeneous (that is, soluble) manner. It will, of course, be appreciated that the active catalyst system form in situ if the catalyst and the

5   cocatalyst components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. It is, however, preferred to form the active catalyst in a separate step in a suitable solvent prior to adding the same to the polymerization mixture.

The polymerization conditions for manufacturing the polymers of the present
10   invention are generally those useful in the solution polymerization process, although the application of the present invention is not limited thereto. Gas phase polymerization processes are also believed to be useful, provided the proper catalysts and polymerization conditions are employed.

Fabricated articles made from the novel ethylene polymers may be prepared using
15   all of the conventional polyethylene processing techniques. Useful articles include films (for example, cast, blown and extrusion coated), fibers (for example, staple fibers (including use of a novel ethylene polymer disclosed herein as at least one component comprising at least a portion of the fiber's surface), spunbond fibers or melt blown fibers (using, for example, systems as disclosed in USP 4,340,563, USP 4,663,220, USP 4,668,566, or USP

20   4,322,027), and gel spun fibers (for example, the system disclosed in USP 4,413,110)), both woven and nonwoven fabrics (for example, spunlaced fabrics disclosed in USP 3,485,706) or structures made from such fibers (including, for example, blends of these fibers with other fibers, for example, PET or cotton) and molded articles (for example, made using an injection molding process, a blow molding process or a rotomolding process). The new polymers

25   described herein are also useful for wire and cable coating operations, impact modification, especially at low temperatures, of thermoplastic olefins (for example, polypropylene), as well as in sheet extrusion for vacuum forming operations, closed cell and open cell foams (including radiation and chemically crosslinked foams and foam structures), and adhesives.

Useful compositions are also suitably prepared comprising the substantially linear
30   polymers of the present invention and at least one other natural or synthetic polymer. Preferred other polymers include thermoplastics such as styrene-butadiene block copolymers, polystyrene (including high impact polystyrene), ethylene vinyl acetate copolymers, ethylene acrylic acid copolymers, other olefin copolymers (especially polyethylene copolymers) and homopolymers (for example, those polyethylene copolymers

35   and homopolymers made using conventional heterogeneous catalysts). Examples of such heterogeneous polyethylene polymers and copolymers include polymers made by the process of USP 4,076,698, other linear or substantially linear polymers of the present invention, and mixtures thereof. Other substantially linear polymers of the present

-26-

invention and conventional heterogeneously branched HDPE and/or heterogeneously branched LLDPE are preferred for use in the thermoplastic compositions.

The compositions comprising the substantially linear ethylene polymers are formed by any convenient method, including dry blending the individual components and

5   subsequently melt mixing, either directly in the extruder used to make the finished article (for example, film), or by pre-melt mixing in a separate extruder. The polyethylene compositions may also be prepared by multiple reactor polymerization techniques. For example, one reactor may polymerize the constrained geometry catalyzed polyethylene and another reactor polymerize the heterogeneous catalyzed polyethylene, either in series

10   or in parallel operation.

Compositions comprising the ethylene polymers can also be formed into fabricated articles such as those previously mentioned using conventional polyethylene processing techniques which are well known to those skilled in the art of polyethylene processing.

For examples described herein, unless otherwise stipulated, all procedures were

15   performed under an inert atmosphere of nitrogen or argon. Solvent choices were often optional, for example, in most cases either pentane or 30-60 petroleum ether can be interchanged. Amines, silanes, lithium reagents, and Grignard reagents were purchased from Aldrich Chemical Company. Published methods for preparing tetramethylcyclopentadiene ($C_5Me_4H_2$) and lithium tetramethylcyclopentadienide

20   ($Li(C_5Me_4H)$) include C. M. Fendrick et al. Organometallics, 3, 819 (1984). Lithiated substituted cyclopentadienyl compounds may be typically prepared from the corresponding cyclopentadiene and a lithium reagent such as n-butyl lithium. Titanium trichloride ($TiCl_3$) was purchased from Aldrich Chemical Company. The tetrahydrofuran adduct of titanium trichloride, $TiCl_3(THF)_3$, was prepared by refluxing $TiCl_3$ in THF overnight,

25   cooling, and isolating the blue solid product, according to the procedure of L. E. Manzer, Inorg. Syn., 21, 135 (1982).

Examples 1-4

The metal complex solution for Example 1 was prepared as follows:

30

Part 1: Prep of $Li(C_5Me_4H)$

In the drybox, a 3L 3-necked flask was charged with 18.34 g of $C_5Me_4H_2$, 800 mL of pentane, and 500 mL of ether. The flask was topped with a reflux condenser, a mechanical stirrer, and a constant addition funnel container 63 mL of 2.5 M n-BuLi in hexane. The BuLi

35   was added dropwise over several hours. A very thick precipitate formed; approx. 1000 mL of additional pentane had to be added over the course of the reaction to allow stirring to continue. After the addition was complete, the mixture was stirred overnight. The next day, the material was filtered, and the solid was thoroughly washed with pentane and then dried under reduced pressure. 14.89 g of $Li(C_5Me_4H)$ was obtained (78 percent).

-27-

Part 2: Prep of $C_5Me_4HSiMe_2Cl$

In the drybox 30.0 g of $Li(C_5Me_4H)$ was placed in a 500 mL Schlenk flask with 250 mL of THF and a large magnetic stir bar. A syringe was charged with 30 mL of Me_2SiCl_2 and the flask and syringe were removed from the drybox. On the Schlenk line under a flow of argon, the flask was cooled to -78°C, and the Me_2SiCl_2 added in one rapid addition. The reaction was allowed to slowly warm to room temperature and stirred overnight. The next morning the volatile materials were removed under reduced pressure, and the flask was taken into the drybox. The oily material was extracted with pentane, filtered, and the pentane was removed under reduced pressure to leave the $C_5Me_4HSiMe_2Cl$ as a clear yellow liquid (46.83 g; 92.9 percent).

Part 3: Prep of $C_5Me_4HSiMe_2NH^tBu$

In the drybox, a 3-necked 2 L flask was charged with 37.4 g of t-butylamine and 210 mL of THF. $C_5Me_4HSiMe_2Cl$ (25.47 g) was slowly dripped into the solution over 3-4 hours. The solution turned cloudy and yellow. The mixture was stirred overnight and the volatile materials removed under reduced pressure. The residue was extracted with diethyl ether, the solution was filtered, and the ether removed under reduced pressure to leave the $C_5Me_4HSiMe_2NH^tBu$ as a clear yellow liquid (26.96 g; 90.8 percent).

Part 4: Prep of $[MgCl]_2[Me_4C_5SiMe_2N^tBu](THF)_x$

In the drybox, 14.0 mL of 2.0 M isopropylmagnesium chloride in ether was syringed into a 250 mL flask. The ether was removed under reduced pressure to leave a colorless oil. 50 mL of a 4:1 (by volume) toluene:THF mixture was added followed by 3.50 g of $Me_4HC_5SiMe_2NH^tBu$. The solution was heated to reflux. After refluxing for 2 days, the solution was cooled and the volatile materials removed under reduced pressure. The white solid residue was slurried in pentane and filtered to leave a white powder, which was washed with pentane and dried under reduced pressure. The white powder was identified as $[MgCl]_2[Me_4C_5SiMe_2N^tBu](THF)_x$ (yield: 6.7 g).

Part 5: Prep of $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$

In the drybox, 0.50 g of $TiCl_3(THF)_3$ was suspended in 10 mL of THF. 0.69 g of solid $[MgCl]_2[Me_4C_5SiMe_2N^tBu](THF)_x$ was added, resulting in a color change from pale blue to deep purple. After 15 minutes, 0.35 g of AgCl was added to the solution. The color immediately began to lighten to a pale green/yellow. After 1.5 hours, the THF was removed under reduced pressure to leave a yellow-green solid. Toluene (20 mL) was added, the solution was filtered, and the toluene was removed under reduced pressure to leave a yellow-green solid, 0.51 g (quantitative yield) identified by 1H NMR as $[C_5Me_4(SiMe_2N^tBu)]TiCl_2$.

-28-

Part 6: Preparation of [C$_5$Me$_4$(SiMe$_2$N^{t}Bu)]TiMe$_2$

In an inert atmosphere glove box, 9.031 g of [C$_5$Me$_4$(Me$_2$SiN^{t}Bu)]TiCl$_2$ was charged into a 250 ml flask and dissolved into 100 ml of THF. This solution was cooled to about -25°C by placement in the glove box freezer for 15 minutes. To the cooled solution was added 35 ml of a 1.4 M MeMgBr solution in toluene/THF (75/25). The reaction mixture was stirred for 20 to 25 minutes followed by removal of the solvent under vacuum. The resulting solid was dried under vacuum for several hours. The product was extracted with pentane (4x50 ml) and filtered. The filtrate was combined and the pentane removed under vacuum giving the catalyst as a straw yellow solid.

The metal complex, [C$_5$Me$_4$(SiMe$_2$N^{t}Bu)]TiMe$_2$, solution for Examples 2 and 3 was prepared as follows:

In an inert atmosphere glove box 10.6769 g of a tetrahydrofuran adduct of titanium trichloride, TiCl$_3$(THF)$_3$, was loaded into a 1 L flask and slurried into 300 ml of THF. To this slurry, at room temperature, was added 17.402 g of [MgCl]$_2$ [N^{t}BuSiMe$_2$C$_5$Me$_4$] (THF)$_x$ as a solid. An additional 200 ml of THF is used to help wash this solid into the reaction flask. This addition resulted in an immediate reaction giving a deep purple solution. After stirring for 5 minutes 9.23 ml of a 1.56 M solution of CH$_2$Cl$_2$ in THF was added giving a quick color change to dark yellow. This stage of the reaction was allowed to stir for about 20 to 30 minutes. Next, 61.8 ml of a 1.4 M MeMgBr solution in toluene/THF(75/25) was added via syringe. After about 20 to 30 minutes stirring time the solvent was removed under vacuum and the solid dried. The product was extracted with pentane (8x50ml) and filtered. The filtrate was combined and the pentane removed under vacuum giving the metal complex as a tan solid.

The metal complex, [C$_5$Me$_4$(SiMe$_2$N^{t}Bu)]TiMe$_2$, solution for Example 4 was prepared as follows:

In an inert atmosphere glove box 4.8108 g of TiCl$_3$(THF)$_3$ was placed in a 500 ml flask and slurried into 130 ml of THF. In a separate flask 8.000 g of [MgCl]$_2$[N^{t}BuSiMe$_2$C$_5$Me$_4$](THF)$_x$ was dissolved into 150 ml of THF. These flasks were removed from the glove box and attached to a vacuum line and the contents cooled to -30°C. The THF solution of [MgCl]$_2$[N^{t}BuSiMe$_2$C$_5$Me$_4$](THF)$_x$ was transferred (over a 15 minute period) via cannula to the flask containing the TiCl$_3$(THF)$_3$ slurry. This reaction was allowed to stir for 1.5 hours over which time the temperature warmed to 0°C and the solution color turned deep purple. The reaction mixture was cooled back to -30°C and 4.16 ml of a 1.56 M CH$_2$Cl$_2$ solution in THF was added. This stage of the reaction was stirred for an additional 1.5 hours and the temperature warmed to -10°C. Next, the reaction mixture was again cooled to -40°C and 27.81 ml of a 1.4 M MeMgBr solution in toluene/THF (75/25) was

-29-

added via syringe and the reaction was allowed to warm slowly to room temperature over 3 hours. After this time the solvent was removed under vacuum and the solid dried. At this point the reaction flask was brought back into the glove box where the product was extracted with pentane (4x50 ml) and filtered. The filtrate was combined and the pentane removed under vacuum giving the catalyst as a tan solid. The metal complex was then dissolved into a mixture of C_8-C_{10} saturated hydrocarbons (for example, Isopar™ E, made by Exxon) and ready for use in polymerization.

Polymerization

The polymer products of Examples 1-4 were produced in a solution polymerization process using a continuously stirred reactor. Additives (for example, antioxidants, pigments, etc.) can be incorporated into the interpolymer products either during the pelletization step or after manufacture, with a subsequent re-extrusion. Examples 1-4 were each stabilized with 1250 ppm calcium stearate, 200 ppm Irganox 1010, and 1600 ppm Irgafos 168. Irgafos™ 168 is a phosphite stabilizer and Irganox™ 1010 is a hindered polyphenol stabilizer (for example, tetrakis [methylene 3-(3,5-ditert.butyl-4-hydroxyphenylpropionate)]methane). Both are trademarks of and made by Ciba-Geigy Corporation. A representative schematic for the polymerization process is shown in Figure 1.

The ethylene (4) and the hydrogen were combined into one stream (15) before being introduced into the diluent mixture (3). Typically, the diluent mixture comprises a mixture of C_8-C_{10} saturated hydrocarbons (1), (for example, Isopar™ E, made by Exxon) and the comonomer(s) (2). For Example 1, the comonomer is 1-octene. The reactor feed mixture (6) was continuously injected into the reactor (9). The metal complex (7) and the cocatalyst (8) (the cocatalyst is tris(pentafluorophenyl)borane for Examples 1-4 herein which forms the ionic catalyst in situ) were combined into a single stream and also continuously injected into the reactor. Sufficient residence time was allowed for the metal complex and cocatalyst to react to the desired extent for use in the polymerization reactions, at least about 10 seconds. For the polymerization reactions of Examples 1-4, the reactor pressure was held constant at about 3.48 MPa (490 psig). Ethylene content of the reactor, after reaching steady state, was maintained below about 8 percent.

After polymerization, the reactor exit stream (14) was introduced into a separator (10) where the molten polymer was separated from the unreacted comonomer(s), unreacted ethylene, unreacted hydrogen, and diluent mixture stream (13). The molten polymer was subsequently strand chopped or pelletized and, after being cooled in a water bath or pelletizer (11), the solid pellets were collected (12). Table 1 describes the polymerization conditions and the resultant polymer properties:

Table I

Example	1*	2	3	4
Ethylene feed rate, kg/hr (lbs/hour)	1.5 (3.2)	1.7 (3.8)	1.7 (3.8)	1.7 (3.8)
Comonomer/Total Olefin ratio*, mole percent	12.3	0	0	0
Hydrogen/ethylene ratio, mole percent	0.054	0.072	0.083	0.019
Diluent/ethylene ratio, weight basis	9.5	7.4	8.7	8.7
Metal complex conc., molar	0.00025	0.0005	0.001	0.001
Metal complex flow rate, ml/min	5.9	1.7	2.4	4.8
Cocatalyst conc., molar	0.001	0.001	0.002	0.002
Cocatalyst flow rate, ml/min	2.9	1.3	6	11.9
Reactor temp, °C	114	160	160	200
Polymer conc. in the reactor exit stream, weight percent	7.1	8.4	9.5	8.4
Comonomer conc. in the reactor exit stream, weight percent	3.8	0	0	0
Ethylene conc. in the reactor exit stream, weight percent	2.65	3.59	0.86	1.98
Product I_2, g/10 minutes	1.22	0.96	1.18	0.25
Product density, g/cm^3	0.903	0.954	0.954	0.953
Product I_{10}/I_2	6.5	7.4	11.8	16.1
Single DSC Melting Peak, °C	97	132	131	132
Product M_w	95,400	93,800	71,600	105,800
Product M_n	50,000	48,200	34,200	51,100
Product M_w/M_n	1.91	1.95	2.09	2.07
Ethylene Conversion, percent	71	70	92	81
LCB/Chain	N.M.**	—	0.53	0.66
LCB/10,000 Carbons	N.M.**	—	2.2	1.8
Aluminium Residue, ppm	0	0	0	0

*For Example 1, the Comonomer/Total Olefin ratio is defined as

5   the percentage molar ratio of 1-octene/(1-octene + ethylene). Ex. 1* is a Comparative Example since the copolymer

has onset of gross melt fracture less than 4 x 10^6 dyne/cm^2.

**N.M. = Not Measured.

-31-

The ^{13}C NMR spectrum of Example 3 (ethylene homopolymer) shows peaks which can be assigned to the $\alpha\delta^+$, $\beta\delta^+$ and methine carbons associated with a long chain branch. Long chain branching was determined using the method of Randall described earlier in this disclosure, wherein he states that "Detection of these resonances in high-density

5 polyethylenes where no 1-olefins were added during the polymerization should be strongly indicative of the presence of long chain branching." Using the equation 141 from Randall (p. 292):

Branches per 10,000 carbons = $[(1/3)(\alpha)/T_{Tot}] \times 10^4$,

10

wherein α = the average intensity of a carbon from a branch ($\alpha\delta^+$) carbon and T_{Tot} = the total carbon intensity. The number of long chain branches in this sample was determined to be 3.4 per 10,000 total carbon atoms, or 0.34 long chain branches/1000 total carbon atoms using 300 MHz ^{13}C NMR, and 2.2 per 10,000 total carbon atoms, or 0.22 long chain

15 branches/1000 total carbon atoms using a 600 MHz ^{13}C NMR.

Examples 5, 6 and Comparative Examples 7-9

Examples 5, 6 and Comparison Examples 7-9 with the same melt index were tested for rheology Comparison. Examples 5 and 6 were the substantially linear

20 ethylene/1-octene copolymers produced by the constrained geometry catalyst technology, as described in Example 1, with the exception that lower ethylene concentrations were used for Examples 5 and 6 providing for higher I_{10}/I_2 ratios and consequently more long chain branching than Example 1. Examples 5 and 6 are stabilized as Examples 1-4. Comparison Examples 7, 8 and 9 were conventional heterogeneous Ziegler polymerization blown film

25 resins Dowlex™ 2045A, Attane™ 4201, and Attane™ 4403, respectively, all of which are ethylene/1-octene copolymers made by The Dow Chemical Company.

Comparative Example 7 was stablized with 200 ppm Irganox™ 1010, and 1600 ppm Irgafos™ 168 while Comparative Examples 8 and 9 were stablized with 200 ppm Irganox™ 1010 and 800 ppm PEPQ™. PEPQ™ is a trademark of Sandoz Chemical, the primary

30 ingredient of which is believed to be tetrakis-(2,4-di-tertbutyl-phenyl)-4,4' biphenylphosphonite. A comparison of the physical properties of each Example and Comparative Example is listed in Table II.

-32-

Table II

Property	Ex. 5	Ex. 6	Comparative Example 7	Comparative Example 8	Comparative Example 9
I_2, g/10 minutes	1	1	1	1	0.76
Density, g/cm^3	0.92	0.902	0.92	0.912	0.905
I_{10}/I_2	9.45	7.61	7.8 - 8	8.2	8.7
Product M_w	73,800	96,900	124,600	122,500	135,300
Product M_n	37,400	46,400	34,300	32,500	31,900
Product M_w/M_n	1.97	2.09	3.5 - 3.8	3.8	3.8 - 4.2
DSC Melt Peak(s), °C	111	95	114, 118, 122	100, 116, 121	96, 116, 121

Surprisingly, even though the molecular weight distribution of Examples 5 and 6 was narrow (that is, M_w/M_n is low), the I_{10}/I_2 values were comparable or higher in comparison with Comparative Examples 7-9. A comparison of the relationship between I_{10}/I_2 vs. M_w/M_n for some of the novel polymers described herein and conventional heterogeneous Ziegler polymers is given in Figure 2. The I_{10}/I_2 value for the novel polymers of the present invention was essentially independent of the molecular weight distribution, M_w/M_n which is not true for conventional Ziegler polymerized resins.

Example 5 and Comparative Example 7 with similar melt index and density (Table II) were also extruded via a Gas Extrusion Rheometer (GER) at 190°C using a 752 micrometers (0.0296 inch) diameter, 20:1 L/D die. The processing index (P.I.) was measured at an apparent shear stress of 2.15×10^6 dyne/cm^2 as described previously. The onset of gross melt fracture can easily be identified from the shear stress vs. shear rate plot shown in Figure 3 where a sudden jump of shear rate occurs. A comparison of the shear stresses and corresponding shear rates before the onset of gross melt fracture is listed in Table III. It is particularly interesting that the PI of Example 5 was more than 20 percent lower than the PI of Comparative Example 7 and that the onset of melt fracture or sharkskin for Example 5 was also at a significantly higher shear stress and shear rate in comparison with the Comparative Example 7. Furthermore, the Melt Tension (MT) as well as Elastic Modulus of Example 5 were higher than that of Comparative Example 7.

Note that each of the Comparative Examples 7-9 had three distinct melting peaks as measured by DSC, which is evidence of their heterogeneous branching distribution. In contrast, the polymers of Examples 5 and 6 had a single melting peak as measured by DSC between the temperatures of -30 and 150°C which is evidence of the homogeneity of the polymers branching distribution. Furthermore, the single melting peaks of Examples 5 and 6 indicate that each polymer was not a "blend" unlike the polymers disclosed in USP 5,218,071.

-33-

Table III

Property	Example 5	Comparative Example 7
I_2 (g/10 minutes)	1	1
I_{10}/I_2	9.45	7.8 - 8
PI (kpoise)	11	15
Melt tension (gms)	1.89	1.21
Elastic modulus at 0.1 rad/sec (dynes/cm²)	2425	882.6
OGMF*, critical shear rate (1/sec)	>1556 (not observed)	936
OGMF*, critical shear stress (MPa)	≥0.452 (not observed)	0.366
OSMF**, critical shear rate (1/sec)	>1566 (not observed)	about 628
OSMF**, critical shear stress (MPa)	≥0.452 (not observed)	about 0.25

*Onset of Gross Melt Fracture.

**Onset of Surface Melt Fracture.

Example 6 and Comparison Example 9 had similar melt index and density, but Example 6 had lower I_{10}/I_2 (Table IV). These polymers were extruded via a Gas Extrusion Rheometer (GER) at 190°C using a 752 micrometers (0.0296 inch) diameter, 20:1 L/D die. The processing index (PI) was measured at an apparent shear stress of 2.15×10^6 dyne/cm² as described previously.

Table IV

Property	Example 6	Comparative Example 9
I_2 (g/10 minutes)	1	0.76
I_{10}/I_2	7.61	8.7
PI (kpoise)	14	15
Melt tension (gms)	1.46	1.39
Elastic modulus at 0.1 rad/sec (dynes/cm^2)	1481	1921
OGMF*, critical shear rate (1/sec)	1186	652
OGMF*, critical shear stress (MPa)	0.431	0.323
OSMF**, critical shear rate (1/sec)	about 764	about 402
OSMF**, critical shear stress (MPa)	0.366	0.280

*Onset of Gross Melt Fracture.

5   **Onset of Surface Melt Fracture.

The onset of gross melt fracture can easily be identified from the shear stress vs. shear rate plot shown in Figure 4 where a sudden increase of shear rate occurs at an apparent shear stress of about 3.23×10^6 dyne/cm^2 (0.323 MPa). A comparison of the critical shear stresses

10   and corresponding critical shear rates at the onset of gross melt fracture is listed in Table IV. The PI of Example 6 is surprisingly about the same as Comparative Example 9, even though the I_{10}/I_2 is lower for Example 6. The onset of melt fracture or sharkskin for Example 6 is also at a significantly higher shear stress and shear rate in comparison with the Comparative Example 9. Furthermore, it is also unexpected that the Melt Tension (MT)

15   of Example 6 is higher than that of Comparative Example 9, even though the melt index for Example 6 is slightly higher and the I_{10}/I_2 is slightly lower than that of Comparative Example 9.

Comparative Examples 10-19

20   Batch ethylene/1-octene polymerizations were conducted under the following conditions:

Preparation of $[HNEt_3]+[MeB(C_6F_5)_3]-$

A 100 ml flask was charged with 1.00 gram of tris(pentafluorophenyl)boron (1.95 mmol) and 70 ml of anhydrous pentane. After dissolution, 1.5 ml of MeLi (1.4 M in diethyl

25   ether, 2.1 mmol, 1.07 equiv) was added at 25°C via syringe. A milky white mixture formed

-35-

immediately and, after several minutes, two phases formed. The mixture was stirred for 15 hr and then the upper layer decanted. The viscous lower layer was washed twice with 30 ml of pentane and concentrated in vacuo for 2 hours to give a clear, colorless, viscous oil. Under nitrogen, the oil was quenched with a 40 ml of an aqueous 0.5 M $HNEt_3Cl$ solution (20

5   mmol, 10 equiv) which had previously been cooled to 0°C. A white, gooey precipitate formed instantly. After two minutes, the solid was collected by filtration and washed twice with 20 ml of 0.5 M $HNEt_3Cl$ solution followed by two washings with distilled water. The solid was dehydrated under high vacuum at 25°C for 15 hours to give a powdery white solid (0.77 grams, 63 percent) which was identified as the desired

10   triethylammonium tris(pentafluorophenyl)methylborate salt.

Preparation of $[HNEt_3]+[(allyl)B(C_6F_5)3]-$

A 100 ml flask was charged with 1.00 gram of tris(pentafluorophenyl)boron (1.95 mmol) and 40 ml of anhydrous pentane. After dissolution, 2.05 ml of (allyl)MgBr (1.0 M in

15   diethyl ether, 2.05 mmol, 1.05 equiv) was added at 25°C via syringe. A cloudy white mixture formed immediately and, after several minutes, two phases formed. The mixture was stirred for 15 hr and then the upper layer decanted. The viscous lower layer was washed twice with 30 ml of pentane and concentrated in vacuo for 2 hours to give a clear, colorless, viscous oil. Under nitrogen, the oil was quenched with a 40 ml of an aqueous 0.5 M

20   $HNEt_3Cl$ solution (20 mmol, 10 equiv) which had previously been cooled to 0°C. A gooey, white precipitate formed after several minutes. The solid was collected by filtration and washed twice with 20 ml of 0.5 M $HNEt_3Cl$ solution followed by two washings with distilled water. The solid was dehydrated under high vacuum at 25°C for 15 hours to give a pasty white solid (0.39 grams, 30 percent) which was identified as the desired

25   triethylammonium tris(pentafluorophenyl)allylborate salt.

Batch Reactor Polymerization Procedure

A 2 L stirred autoclave was charged with the desired amounts of a mixed alkane solvent (Isopar® E, available from Exxon Chemicals, Inc.) and 1-octene comonomer. The

30   reactor was heated to the polymerization temperature. Hydrogen was added by differential pressure expansion from a 75 ml addition tank.

The term "hydrogen delta psi" in Table 1 represents the difference in pressure between the starting and final pressure in the hydrogen addition tank after adding hydrogen to the 2L reactor containing a total of approximately 1200 ml of solvent and

35   1-octene. The reactor was heated to the polymerization temperature and was saturated with ethylene to the desired pressure. For these experiments, a constant ethylene/solvent pressure of about 3.55 MPa (500 psig) at a temperature of 140°C corresponds to an ethylene concentration of about 8.4 percent by weight of the reactor contents. Metal complex and cocatalyst were mixed in a drybox by syringing the desired amount of 0.0050 M metal

complex solution (in Isopar® E or toluene) into a solution of the cocatalyst (in Isopar® E or toluene). This solution was then transferred to a catalyst addition tank and injected into the reactor. The polymerization was allowed to proceed for the desired time and then the solution was drained from the bottom of the reactor and quenched with isopropanol. About

5   100 mg of a hindered phenolic antioxidant (Irganox® 1010, available from Ciba-Geigy corporation) was added and the polymer was air dried overnight. The residual solvent was removed in a vacuum oven overnight. The results are shown in Table V and VA:

Table V

10

Comp. Ex.	H$_2$, kPa (psi)	1-octene (gms)	Isopar E (gms)	yield (gms)	Effcny. (gm/gm Ti)	Aluminum (ppm)
10A*	344 (50)	38	820	39.6	330,689	0
11A*	172 (25)	38	820	70.1	390,257	0
12A*	241 (35)	38	820	46.4	258,316	0
13A*	207 (30)	38	820	48.8	271,677	0
14A*	241 (35)	30	828	52.1	290,049	0
15A*	186 (27)	38	820	36.5	152,401	0
16A**	179 (26)	38	820	47.8	266,110	0
17B***	241 (35)	40	818	19.7	41,127	6850
18B***	344 (50)	40	818	19.7	41,127	6850
19B***	172 (25)	40	818	18.3	38,204	7380

A = metal complex of [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)] TiMe$_2$ (as in USP 5,064,802)

B = metal complex of [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)] TiCl$_2$ (as in USP 5,026,798)

* = Cocatalyst of [Et$_3$NH] + [(allyl)B(C$_6$F$_5$)$_3$]- (as in USP '802)

15   ** = Cocatalyst of [Et$_3$NH] + [(Me)B(C$_6$F$_5$)$_3$]- (as in USP '802)

*** = methyl aluminoxane (MAO) (as in USP '798)

Reactor temperature is constant at about 140°C

Ethylene/solvent pressure is constant at about 3.55 MPa (500 psig)

Run time is about 15 minutes

20

Table VA

Comp. Ex.	µmoles complex	µmoles cocatalyst	Irganox 1010 (ppm)
10A*	2.5	2.5	2500
11A*	3.75	3.75	1400
12A*	3.75	3.75	2200
13A*	3.75	3.75	2000
14A*	3.75	3.75	1900
15A*	5	5	2700
16A*	3.75	3.75	2000
17B***	10	5000	5000
18B***	10	5000	5000
19B***	10	5000	5500

A = metal complex of [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)] TiMe$_2$ (as in USP 5,064,802)

B = metal complex of [(C$_5$Me$_4$)SiMe$_2$N(t-Bu)] TiCl$_2$ (as in USP 5,026,798)

* = Cocatalyst of [Et$_3$NH] + [(allyl)B(C$_6$F$_5$)$_3$]- (as in USP '802)

** = Cocatalyst of [Et$_3$NH] + [(Me)B(C$_6$F$_5$)$_3$]- (as in USP '802)

*** = methyl aluminoxane (MAO) (as in USP '798)

Reactor temperature is constant at about 140°C

Ethylene/solvent pressure is constant at about 3.55 MPa (500 psig)

Run time is about 15 minutes

The samples were each extruded via a Gas Extrusion Rheometer (GER) at 190°C using 0.0296 inch (752 micrometers) diameter die (preferably 0.0143 inch (363 micrometers) diameter die for high flow polymers, for example 50-100 MI or greater) having L/D of 20:1 and entrance angle of 180 degrees, as shown in the attached drawing. The OGMF can easily be identified from the shear stress vs. shear rate plot where a sudden jump of shear rate occurs or when the surface of the extrudate becomes very rough or irregular, or from deep ridges which can be clearly detected by visual observation. OSMF is characterized by fine scale surface irregularities ranging from loss of surface gloss to the more severe form of matte or sharkskin which can easily be seen using microscopy at a magnification of 40X.

Table VI displays the test results from Comparative Examples 10-19:

Table VI

Comp. Ex.	I_2 (gm/10 min)	I_{10}/I_2	(I_{10}/I_2) - 4.63	Measured M_w/M_n	OGMF* Shear Rate (sec^{-1})	OGMF* Shear Stress (MPa)
10	4.52	5.62	0.99	1.856	706	0.344
11	0.67	6.39	1.76	1.834	118	0.323
12	2.24	5.62	0.99	1.829	300	0.323
13	2.86	5.60	0.97	1.722	397	0.323
14	3.25	5.66	1.03	1.827	445	0.302
15	1.31	5.67	1.04	1.718	227	0.302
16	1.97	5.7	1.07	1.763	275	0.302
17	0.36	12.98	8.35	5.934	<29	<0.086
18	0.40	13.34	8.71	5.148	<11.08	<0.086
19	0.13	13.25	8.62	6.824	<10.39	<0.086

Comparative Examples 10 - 16 were prepared using the catalyst composition as described in U.S. Patent 5,064,802 (Stevens et al.), as described above. Comparative Examples 17 - 19 were prepared using the catalyst composition described in U.S. Patent 5,026,798 (Canich), as described above. All of the Comparative Polymer Examples made using a batch reactor at an ethylene concentration of about 8.4 percent by weight of the reactor contents or more tested had onset of gross melt fracture at a shear stress of less than or equal to 0.344 MPa (3.44 x 10^6 dyne/cm^2).

Interestingly, an ethylene concentration of about 8.4 percent is considered to be on the low side for a batch polymerization procedure, since it limits the reaction kinetics and slows the polymerization process. Increasing the ethylene concentration in a batch reactor, as is taught in U.S. Patent 5,026,798 (Canich), where the calculated propylene reactor concentrations for these ten examples ranges from a low of about 12.6 percent (Example 1) to a high of about 79 percent (Example 6), by weight of the reactor contents, results in polymerization of polymers which do not have the novel structure discovered by Applicants, as the OGMF data in Table VI demonstrates. Furthermore, the I_{10}/I_2 ratio of such comparative polymers made using a batch reactor at relatively high ethylene concentrations increases as the molecular weight distribution, M_w/M_n, increases, as is expected based on conventional Ziegler polymerized polymers.

Example 20 and Comparative Example 21

Blown film was fabricated from the two novel ethylene/1-octene polymers of Examples 5 and 6 made in accordance with the present invention and from two comparative conventional polymers made according to conventional Ziegler catalysis. The blown films were tested for physical properties, including heat seal strength versus heat seal temperature (shown in Figure 5 for Examples 20 and 22 and Comparative Examples 21 and 23), machine (MD) and cross direction (CD) properties (for example, tensile yield and break, elongation at break and Young's modulus). Other film properties such as dart, puncture, tear, clarity, haze, 20 degree gloss and block were also tested.

Blown Film Fabrication Conditions

The improved processing substantially linear polymers of the present invention produced via the procedure described earlier, as well as two comparative resins were fabricated on an Egan blown film line using the following fabrication conditions:

- 2 inch (5 cm) diameter extruder
- 3 inch (7.6 cm) die
- 30 mil die gap
- 25 RPM extruder speed
- 460°F (238°C) melt temperature
- 1 mil gauge
- 2.7:1 Blow up ratio (12.5 inches (31.7 cm) layflat)
- 12.5 inches (31.7 cm) frost line height

The melt temperature was kept constant by changing the extruder temperature profile. Frost line height was maintained at 12.5 inches (31.7 cm) by adjusting the cooling air flow. The extruder output rate, back pressure and power consumption in amps were monitored throughout the experiment. The polymers of the present invention and the comparative polymers were all ethylene/1-octene copolymers. Table VII summarizes physical properties of the two polymers of the invention and for the two comparative polymers:

Table VII

Property	Example 20	Comparative Example 21	Example 22	Comparative Example 23
I_2 (g/10 minutes)	1	1	1	0.8
Density (g/cm^3)	0.92	0.92	0.902	0.905
I_{10}/I_2	9.45	about 8	7.61	8.7
M_w/M_n	1.97	about 4	2.09	about 5

Tables VIII and IX summarize the film properties measured for blown film made from two of these four polymers:

Table VIII

Blown film properties

Property	Example 20 MD	Example 20 CD	Comparative Example 21 MD	Comparative Example 21 CD
Tensile yield, MPa (psi)	9.59 (1391)	9.24 (1340)	10.4 (1509)	10.98 (1593)
Tensile break, MPa (psi)	49.6 (7194)	40.41 (5861)	46.18 (6698)	47.26 (6854)
Elongation, percent	650	668	631	723
Young's modulus, MPa (psi)	130.9 (18,990)	137.8 (19,997)	159.2 (23,086)	162.2 (23,524)
PPT* tear, gms	5.9	6.8	6.4	6.5

*Puncture Propagation Tear
MD = machine direction
CD = cross direction

Table IX

Property	Example 20	Comparative Example 21
Dart A, grams	472	454
Puncture, grams	235	275
Clarity, percent transmittance	71	68
Haze, percent	3.1	6.4
20 degree gloss	114	81
Block, grams	148	134

During the blown film fabrication, it was noticed that at the same screw speed (25 rpm) and at the same temperature profile, the extruder back pressure was about 24.1 MPa (3500 psi) at about 58 amps power consumption for Comparative Example 21 and about 17.6 MPa (2550 psi) at about 48 amps power consumption for Example 20, thus showing the novel polymer of Example 20 to have improved processability over that of a conventional heterogeneous Ziegler polymerized polymer. The throughput was also higher for Example 20 than for Comparative Example 21 at the same screw speed. Thus, Example 20 had higher pumping efficiency than Comparative Example 21 (that is, more polymer goes through per turn of the screw).

As Figure 5 shows, the heat seal properties of polymers of the present invention were improved, as evidenced by lower heat seal initiation temperatures and higher heat seal strengths at a given temperature, as compared with conventional heterogeneous polymers at about the same melt index and density.

Examples 24 and 25

The polymer products of Examples 24 and 25 were produced in a continuous solution polymerization process using a continuously stirred reactor, as described in USP 5,272,236. The metal complex $[C_5Me_4(SiMe_2N^tBu)]TiMe_2$ was prepared as described in USP 5,272,236 and the cocatalysts used were tris(pentafluorophenyl) borane (B:Ti ratio of 2:1) and MMAO (Al:Ti ratio of 4:1). For Example 24 the ethylene concentration in the reactor was about 1.10 percent and for Example 25 the ethylene concentration in the reactor was about 1.02 percent (percentages based on the weight of the reactor contents). For each Example, the reactor was run without hydrogen.

Additives (for example, antioxidants, pigments, etc.) can be incorporated into the interpolymer products either during the pelletization step or after manufacture, with a subsequent re-extrusion. Examples 24 and 25 were each stabilized with 1250 ppm Calcium Stearate, 200 ppm Irganox 1010, and 1600 ppm Irgafos 168. Irgafos™ 168 is a phosphite stabilizer and Irganox™ 1010 is a hindered polyphenol stabilizer (for example, tetrakis [methylene 3-(3,5-ditert.butyl-4-hydroxyphenylpropionate)]methane. Both are trademarks of and made by Ciba-Geigy Corporation.

Example 24 and Comparative Example 26

Example 24 was an ethylene/1-octene elastic substantially linear ethylene polymer produced as described herein.

Comparative Example 26 was an ethylene/1-butene copolymer trademarked Exact™ made by Exxon Chemical containing butylated hydroxy toluene (BHT) and

-42-

Irganox[TM] 1076 as polymeric stabilizers. Table X summarizes physical properties and rheological performance of Example 24 and Comparative Example 26:

Table X

Property	Example 24	Comparative Example 26
I_2, g/10 minutes	3.3	3.58
Density, g/cm^3	0.870	0.878
I_{10}/I_2	7.61	5.8
M_w/M_n	1.97	1.95
PI, kPoise	3.2	8.4
Elastic Modulus @ 0.1 rad/sec, dyne/cm^2	87.7	8.3
OSMF*, critical shear rate, sec^{-1}	660	250

*Onset of surface melt fracture

Even though Example 24 and Comparative Example 26 had very similar molecular weight distributions (M_w/M_n), I_2 and density, Example 24 had a much lower processing index (PI) (38 percent of the PI of Comparative Example 26), a much higher shear rate at the onset of surface melt fracture (264 percent of shear rate at onset of OSMF) and an elastic modulus an order of magnitude higher than Comparative Example 26, demonstrating that Example 24 had much better processability and higher melt elasticity than Comparative Example 26.

Elastic modulus is indicative of a polymer's melt stability, for example, more stable bubbles when making blown film and less neck-in during melt extrusion. Resultant physical properties of the finished film are also higher.

Onset of surface melt fracture is easily identified by visually observing the surface extrudate and noting when the extrudate starts losing gloss and small surface roughness is detected by using 40X magnification.

Dynamic shear viscosity of the polymers was also used to show differences between the polymers and measures viscosity change versus shear rate. A Rheometrics Mechanical Spectrometer (Model RMS 800) was used to measure viscosity as a function of shear rate. The RMS 800 was used at 190°C at 15 percent strain and a frequency sweep (that is, from 0.1-100 rad/sec) under a nitrogen purge. The parallel plates were positioned such that they had a gap of about 1.5-2 mm. Data for Example 24 and Comparative Example 26 are listed in Table XI and graphically displayed in Figure 6.

-43-

Table XI

Shear Rate, rad/sec	Dynamic Viscosity, poise, for Example 24	Dynamic Viscosity, poise, for Comparative Example 26
0.1	28290	18990
0.1585	28070	18870
0.2512	27630	18950
0.3981	27140	18870
0.631	26450	18840
1	25560	18800
1.585	24440	18690
2.512	23140	18540
3.981	21700	18310
6.31	20170	17960
10	18530	17440
15.85	16790	16660
25.12	14960	15620
39.81	13070	14310
63.1	11180	12750
100	9280	10960

Surprisingly, Example 24 showed a shear thinning behaviour, even though
5   Example 24 had a narrow molecular weight distribution. In contrast, Comparative
Example 26 showed the expected behaviour of a narrow molecular weight distribution
polymer, with a flatter viscosity/shear rate curve.

Thus, elastic substantially linear ethylene polymers made in accordance with the
present invention (for example Example 24) had lower melt viscosity than a typical narrow
10   molecular weight distribution linear copolymer made by single site catalyst technology at
the melt processing shear rate region of commercial interest. In addition, the novel elastic
substantially linear ethylene polymers had a higher low shear/zero shear viscosity than
the Comparative linear polymer, thus demonstrating that the copolymers of the invention
had higher "green strength" which is useful for forming and maintaining blended
15   compositions such as those used in the wire and cable coating industry, where the
compounded materials must maintain their integrity at low or zero shear without
segregating the components.

Example 25 and Comparative Example 27

Example 25 was an ethylene/1-octene elastic substantially linear ethylene polymer produced in a continuous solution polymerization process as described herein.

Comparative Example 27 was an ethylene/propene copolymer made by Mitsui PetroChemical Corporation and trademarked Tafmer™ P-0480. Table XII summarizes physical properties and rheological performance of these two polymers:

Table XII

Property	Example 25	Comparative Example 27
I_2, g/10 minutes	1.01	1.1
Density, g/cm^3	0.870	0.870
I_{10}/I_2	7.62	6.06
M_w/M_n	1.98	1.90
PI, kPoise	7.9	27.4
Elastic Modulus @ 0.1 rad/sec, dyne/cm^2	964	567.7
OSMF*, critical shear rate, sec^{-1}	781	105

*Onset of surface melt fracture

Even though Example 25 and Comparative Example 27 had similarly narrow molecular weight distributions (M_w/M_n), I_2, and density, Example 25 had a PI which was 28 percent of that of Comparative Example 27, a 743 percent of the shear rate at the onset of surface melt fracture and a higher elastic modulus than Comparative Example 27, demonstrating that Example 24 had much better processability than Comparative Example 27. Onset of surface melt fracture is easily identified by visually observing the surface extrudate and noting when the extrudate starts losing gloss and small surface roughness is detected by using 40X magnification.

Examples 28-37

Examples 28-35 were ethylene/propene copolymers made using the constrained geometry catalyst described herein and in a continuous solution polymerization process. Examples 36 and 37 were ethylene/1-butene copolymers made using the constrained geometry catalyst described herein and in a continuous solution polymerization process. Examples 28-37 each contained approximately 1250 ppm calcium strearate, 200 ppm Irganox™ 1010. These polymers did not, however, contain a secondary antioxidant (for example a phosphite). The low level of phenol (that is 200 ppm Irganox™ 1010) coupled

-45-

with the lack of the secondary antioxidant may have contributed to the lower melt fracture performance of some of the polymers shown in Table XV. It is well known that thermally processing polyethylene polymers, especially in the presence of oxygen, can lead to oxidative crosslinking and extrusion variation, that is melt fracture. Table XIII and XIIIA describe the polymerization conditions and Table XIV describes the resultant polymer physical properties for Examples 28-35:

Table XIII

Ex.	Reactor ethylene conc., weight percent	Estimated reactor PE conc., weight percent	Ethylene flow rate, kg/hr (lbs/hr)	Hydrogen/ ethylene ratio, mole percent
28	5.3	6.0	1.45 (3.19)	0.048
29	4.2	7.3	1.45 (3.19)	0.024
30	4.0	8.9	1.45 (3.19)	0.028
31	3.5	9.3	1.44 (3.18)	0.024
32	2.5	10.6	1.45 (3.20)	0.027
33	2.6	10.7	1.44 (3.18)	0.007
34	1.3	10.5	1.45 (3.19)	0.027
35	1.0	10.9	1.45 (3.19)	0.010

Table XIIIA

Ex.	Reactor temp, °C	Ethylene Conversion, percent	Diluent/ ethylene ratio	Comonomer/olefin ratio*
28	170	51	8.2	25.5
29	172	61	8.1	24.0
30	171	67	7.1	16.6
31	171	71	7.2	20.1
32	170	79	7.1	15.6
33	173	78	7.1	16.7
34	145	88	8.2	17.8
35	158	91	8.2	18.8

*Comonomer/total olefin ratio = percentage weight ratio of propene/(propene + ethylene).

-46-

Table XIV

Ex.	I_2, gms/10 minutes	I_{10}/I_2	Density, gm/cm^3	M_w/M_n
28	1.08	7.8	0.9176	2.00
29	1.02	8.8	0.9173	2.17
30	0.82	9.2	0.9175	2.08
31	0.79	9.4	0.9196	2.04
32	1.01	10.6	0.9217	2.09
33	0.83	12.4	0.9174	2.31
34	0.54	15.2	0.9201	2.12
35	0.62	15.6	0.9185	2.32

5   Figure 7 graphically displays a best fit line drawn through a plot of the I_{10}/I_2
ratio for the ethylene/propene substantially linear polymers of Examples 28-35 as a
function of ethylene concentration in the polymerization reactor. Surprisingly, in contrast
to conventional Ziegler polymerized polymers and in contrast to a batch polymerization
using the same catalyst and relatively high ethylene concentrations, as the ethylene
10   concentration in the reactor decreased using a continuous polymerization process, the I_{10}/I_2
ratio (indicating the amount of long chain branching in the novel substantially linear
polymers) increased, even though the molecular weight distribution, M_w/M_n, remained
very narrow and essentially constant at about 2.

15   Table XV shows the critical shear stress and critical shear rate at OGMF and
OSMF for Examples 28-35:

-47-

Table XV

Example	OSMF	OGMF
28 (shear stress)	2.15×10^6 dyne/cm^2	4.09×10^6 dyne/cm^2
28 (shear rate)	129.8 sec^{-1}	668.34 sec^{-1}
29 (shear stress)	1.94×10^6 dyne/cm^2	4.3×10^6 dyne/cm^2
29 (shear rate)	118.8 sec^{-1}	652.1 sec^{-1}
30 (shear stress)	1.08×10^6 dyne/cm^2	4.3×10^6 dyne/cm^2
30 (shear rate)	86.12 sec^{-1}	650.7 sec^{-1}
31 (shear stress)	1.08×10^6 dyne/cm^2	$>4.3 \times 10^6$ dyne/cm^2
31 (shear rate)	90.45 sec^{-1}	>6.83 sec^{-1}
32 (shear stress)	1.94×10^6 dyne/cm^2	3.66×10^6 dyne/cm^2
32 (shear rate)	178.2 sec^{-1}	673 sec^{-1}
33 (shear stress)	2.15×10^6 dyne/cm^2	about 3.23×10^6 dyne/cm^2
33 (shear rate)	235.7 sec^{-1}	about 591 sec^{-1}
34 (shear stress)	1.94×10^6 dyne/cm^2	3.44×10^6 dyne/cm^2
34 (shear rate)	204.13 sec^{-1}	725.23 sec^{-1}
35 (shear stress)	1.94×10^6 dyne/cm^2	about 3.26×10^6 dyne/cm^2
35 (shear rate)	274.46 sec^{-1}	637.7 sec^{-1}

5   Tables XVI and XVIA describe the polymerization conditions and Table XVII
describes the resultant polymer physical properties for ethylene/1-butene copolymer
Examples 36 and 37:

Table XVI

10

Ex.	Reactor ethylene conc., weight percent	Reactor PE conc., weight percent	Ethylene flow rate, kg/hr (lbs/hr)	Hydrogen/ ethylene ratio, mole percent
36	5.3	5.8	1.45 (3.20)	0.035
37	1.3	10.8	1.45 (3.19)	0.010

Table XVIA

Ex.	Reactor temp, °C	Diluent/ Ethylene Ratio	Ethylene Conversion, percent	Comonomer/ olefin ratio*
36	170	8.1	51	24.2
37	152	8.2	87	17.1

*Comonomer/total olefin ratio = percentage weight ratio of 1-butene/

(1-butene + ethylene).

Table XVII

Ex.	I_2, gms/10 minutes	I_{10}/I_2	Density, gm/cm³	M_w/M_n
36	0.59	7.5	0.9201	2.06
37	1.03	11.4	0.9146	2.22

The data in Tables XVI, XVIA and XVII show that as the ethylene concentration in the reactor decreased while using the constrained geometry catalyst as described herein, the I_{10}/I_2 ratio of the novel substantially linear polymers increased, indicating the amount of long chain branching in the novel polymers, even while the molecular weight distribution, M_w/M_n, of the novel polymers remained narrow at essentially about 2.

Table XVIII shows the critical shear stress and critical shear rate at OGMF and OSMF for Examples 36 and 37:

Table XVIII

Example	OSMF	OGMF
36 (shear stress)	1.94×10^6 dyne/cm²	4.09×10^6 dyne/cm²
36 (shear rate)	52.3 sec⁻¹	234.45 sec⁻¹
37 (shear stress)	1.08×10^6 dyne/cm²	3.01×10^6 dyne/cm²
37 (shear rate)	160.5 sec⁻¹	493.9 sec⁻¹

Comparative Example 38

An ethylene polymer, as described in USP 5,218,071, was polymerized according to the teachings of that patent and tested for melt fracture properties.

All catalyst manipulations were performed under anhydrous, anaerobic conditions in an inert atmosphere box. The solvents, toluene and Isopar™ E, and the comonomer, octene-1, were thoroughly dried and deaerated beore use. Poly(methylalumioxane) (PMAO) was obtained from AKZO Chemicals Inc. as a 1.55 M Al in toluene solution and used as received. The metallocene ethylenebis(indenyl)hafnium dichloride was obtained from Schering A.G. as a solid. This metallocene is known to contain 0.2 weight percent Zirconium contamination. A slurry of the hafnium complex was prepared from this solid (0.253 g; 0.5 mmol; 0.010 M) and 50 mL toluene. The slurry was thoroughly stirred overnight prior to use.

A 3.78 L (one gallon), stirred autoclave reactor was charged with Isopar™ E (2.1 L) and octene-1 (175 mL) and the contents heated to 80°C. Upon reaching temperature, a sample of the PMAO (26.8 mL; 40.0 mmol Al) in toluene was pressured into the reactor from a 75 mL cylinder using a nitrogen flush. After a few minutes, an aliquot of the metallocene slurry (4.0 mL; 0.040 mmol; Al:Hf=1000:1) was flushed into the reactor in a similar manner. Ethylene was continuously supplied to the reactor at a rate of 17 g/min to initiate polymerization. The ethylene flow was maintained for ten minutes and during the latter part of the polymerization the flow rate slowed as the pressure approached a setpoint of 791 Pa (100 psig). After this time, the ethylene supply was shut off and the contents of the reactor transferred by pressure to a glass resin kettle containing a small amount of antioxidant (0.30 g Irgafos™ 168; 0.07 g Irganox™ 1010). The solvent was slowly allowed to evaporate and the polymer obtained form the solution was dried under vacuum at 50°C for 72 h. The yield of the product was 159 g or an efficiency of 3975 g PE/mmol Hf.

The recovered polymer had a $M_w=1.341 \times 10^5$, $M_n=5.65 \times 10^4$, $M_w/M_n=2.373$, density (measured in a gradient column)=0.8745 g/cm^3, $I_2=0.63$ g/10 min., $I_{10}/I_2=15.9$, and had two distinct melting peaks (as shown in Figure 8). The polymer showed two peak melting points, one at 30.56°C and the other at 102.55°C. The polymer also showed two peak crystallization points, one at 9.47°C and the other at 81.61°C.

Melt fracture was determined using the GER at 190°C with a die having a diameter of 0.0145 inches and an L/D=20.

-50-

CLAIMS

1. An ethylene polymer characterized as having:

a) a melt flow ratio, I_{10}/I_2, ≥ 5.63,

b) a molecular weight distribution, M_w/M_n, defined by the equation:

$M_w/M_n \leq (I_{10}/I_2) - 4.63$, and

c) a critical shear stress at onset of gross melt fracture greater than 4×10^6 dyne/cm^2, and

d) a single melting point as determined by differential scanning calorimetry between -30°C and 150°C.

2. An ethylene polymer characterized as having:

a) a melt flow ratio, I_{10}/I_2, ≥ 5.63,

b) a molecular weight distribution, M_w/M_n, defined by the equation:

$M_w/M_n \leq (I_{10}/I_2) - 4.63$, and

c) a critical shear rate at onset of surface melt fracture at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having an I_2, M_w/M_n and density within ten percent of the ethylene polymer, and

d) a single melting point as determined by differential scanning calorimetry between -30°C and 150°C.

3. An ethylene polymer characterized as having:

a) a melt flow ratio, I_{10}/I_2, ≥ 5.63,

b) a molecular weight distribution, M_w/M_n of from about 1.5 to about 2.5, and

c) a single melting peak as determined by DSC between -30°C and 150°C.

4. An ethylene polymer characterized as having:

a) a melt flow ratio, I_{10}/I_2, ≥ 5.63,

b) a molecular weight distribution, M_w/M_n of from about 1.5 to about 2.5,

c) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having an I_2, M_w/M_n and density within ten percent of the ethylene polymer, and

d) a single melting point as determined by differential scanning calorimetry between -30°C and 150°C.

5. An ethylene polymer characterized as having (i) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having an I_2, M_w/M_n and density

within ten percent of the ethylene polymer, and (ii) a single melting point as determined by differential scanning calorimetry between -30°C and 150°C.

---

6. An ethylene polymer characterized in that the ethylene polymer is a substantially linear ethylene polymer having:

(a) from 0.01 to 3 long chain branches/1000 total carbons and

(b) a critical shear stress at onset of gross melt fracture of greater than 4×10^6 dyne/cm^2, and

(c) a single melting point as determined by differential scanning calorimetry between -30°C and 150°C.

7. An ethylene polymer characterized in that the ethylene polymer is a substantially linear ethylene polymer having:

(a) from 0.01 to 3 long chain branches/1000 total carbons,

(b) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having an I_2, M_w/M_n and density within ten percent of the ethylene polymer, and

(c) a single melting point as determined by differential scanning calorimetry between -30°C and 150°C.

8. An ethylene polymer characterized in that the ethylene polymer is a substantially linear ethylene polymer having:

(a) from 0.01 to 3 long chain branches/1000 total carbons,

(b) a melt flow ratio, I_{10}/I_2, ≥ 5.63, and

(c) a molecular weight distribution, M_w/M_n from 1.5 to 2.5, and

d) a single melting point as determined by differential scanning calorimetry between -30°C and 150°C.

9. The ethylene polymer of any of claims 1-8, wherein the ethylene polymer is further characterized as:

(A) an ethylene homopolymer, or

(B) an interpolymer of ethylene with at least one C_4-C_{18} diolefin.

10. The ethylene polymer of any of claims 1-8, wherein the ethylene polymer is further characterized as:

(A) an ethylene homopolymer, or

(B) an interpolymer of ethylene with at least one C_3-C_{20} alpha-olefin.

11. The ethylene polymer of any of Claims 1-7 in which the M_w/M_n is less than 5.

12. The ethylene polymer of any of Claims 1-7 wherein the ethylene polymer has a M_w/M_n less than 3.5.

13. The ethylene polymer of any of Claims 1-7 in which the M_w/M_n is from 1.5 to 2.5.

14. The ethylene polymer of any of Claims 1-7 wherein the ethylene polymer has a M_w/M_n from 1.7 to 2.3.

15. The ethylene polymer of any of Claims 1-5 wherein the ethylene polymer is a substantially linear ethylene polymer having from 0.01 to 3 long chain branches/1000 total carbons.

16. The ethylene polymer of any of Claims 1-8 further characterized as containing less than 20 ppm aluminum.

17. The ethylene polymer of any of Claims 1-8 further characterized as containing less than 10 ppm aluminum.

18. The ethylene polymer of any of Claims 1-8 further characterized as containing less than 5 ppm aluminum.

19. A process of preparing a substantially linear ethylene polymer having a melt flow ratio, $I_{10}/I_2, \geq 5.63$, a molecular weight distribution, M_w/M_n, defined by the equation: $M_w/M_n \leq (I_{10}/I_2) - 4.63$, and a single melting point as determined by differential scanning calorimetry between -30°C and 150°C, said process characterized by continuously contacting ethylene alone or ethylene and one or more C_3-C_{20} alpha-olefins with a catalyst composition under continuous polymerization conditions, wherein said catalyst composition is characterized as:

-53-

(a)

$$
\begin{array}{ccc}
Z & \longrightarrow & Y \\
\diagup & & \mid \\
Cp^* & \longrightarrow & M \\
& & \diagdown \\
& & (X)_n
\end{array}
$$
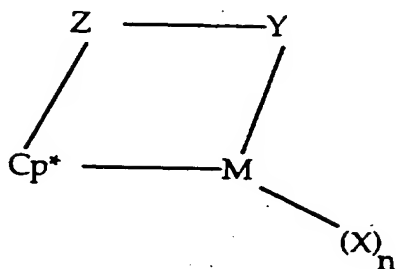
wherein:

M is a metal of group 3-10, or the Lanthanide series of the Periodic Table of the

5   Elements;

Cp* is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 bonding mode to M;

10   Z is a moiety comprising boron, or a member of group 14 of the Periodic Table of the Elements, and optionally sulfur or oxygen, said moiety having up to 20 non-hydrogen atoms, and optionally Cp* and Z together form a fused ring system;

X independently each occurrence is an anionic ligand group or neutral Lewis base

15   ligand group having up to 30 non-hydrogen atoms;

n is 0, 1, 2, 3, or 4 and is 2 less than the valence of M; and

Y is an anionic or nonanionic ligand group bonded to Z and M comprising nitrogen,

20   phosphorus, oxygen or sulfur and having up to 20 non-hydrogen atoms, optionally Y and Z together form a fused ring system, and

(b) an activating cocatalyst.

20. The process of claim 19 wherein (a) corresponds to the formula:
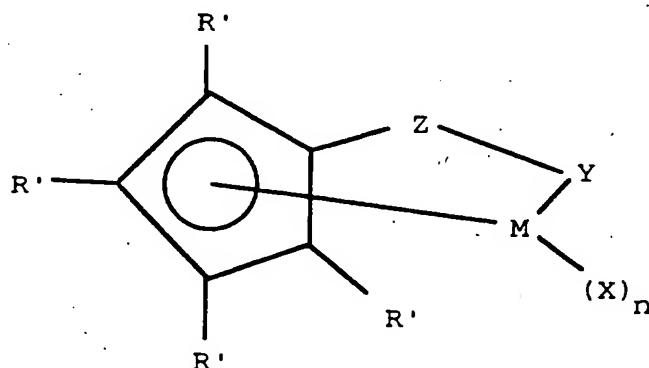
wherein:

R' each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, germyl, cyano, halo and combinations thereof having up to 20 non-hydrogen atoms;

X each occurrence independently is selected from the group consisting of hydride, halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, neutral Lewis base ligands and combinations thereof having up to 20 non-hydrogen atoms;

Y is -O-, -S-, -NR*-, -PR*-, or a neutral two electron donor ligand selected from the group consisting of OR*, SR*, NR*$_2$ or PR*$_2$;

M is a metal of group 3-10, or the Lanthanide series of the Periodic Table of the Elements; and

Z is SiR*$_2$, CR*$_2$, SiR*$_2$SiR*$_2$, CR*$_2$CR*2, CR*=CR*, CR*$_2$SiR*$_2$, GeR*$_2$, BR*, BR*$_2$; wherein

R* each occurrence is independently selected from the group consisting of hydrogen, alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups having up to 20 non-hydrogen atoms, and mixtures thereof, or two or more R* groups from Y, Z, or both Y and Z form a fused ring system; and n is 1 or 2.

21. The process of Claim 19 wherein (a) is an amidosilane or amidoalkanediyl compound corresponding to the formula:

-55-

$$R' \quad (ER'_2)_m \quad N-R'$$
$$M$$
$$(X)_n$$
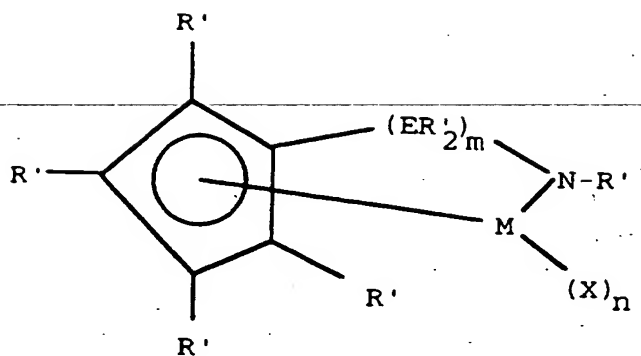
wherein:

M is titanium, zirconium or hafnium, bound in an η^5 bonding mode to the
5   cyclopentadienyl group;

R' each occurrence is independently selected from the group consisting of hydrogen,
silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms;

10   E is silicon or carbon;

X independently each occurrence is hydride, halo, alkyl, aryl, aryloxy or alkoxy of
up to 10 carbons;

15   m is 1 or 2; and

n is 1 or 2.

22. The process of any of the Claims 19-21 in which component (b) is an inert,
20   noncoordinating boron cocatalyst.

23. The process of any of the Claims 19-21 in which the cocatalyst is
tris(pentafluorophenyl)borane.

25   24. The process of any of the Claims 19-21 wherein the process is:
(A) a gas phase process, or
(B) a suspension process, or
(C) a solution process, or
(D) a slurry process.

30

-56-

25. The solution process of Claim 24 wherein the polymerization conditions comprise a reaction temperature and ethylene concentration sufficient to form the substantially linear ethylene polymer.

26. The process of Claim 25 wherein the polymerization conditions comprise a reaction temperature and ethylene concentration sufficient to form a substantially linear ethylene polymer having a I_{10}/I_2 of at least 8.

27. The process of Claim 26 wherein the polymerization conditions comprise a reaction temperature and an ethylene concentration sufficient to form the substantially linear ethylene polymer, wherein the polymer has a I_{10}/I_2 of at least 9.

28. The product obtainable by any of the processes of Claims 19-27.

29. A composition comprising an ethylene polymer and at least one other natural or synthetic polymer, wherein the ethylene polymer is characterized as the ethylene polymer of any of Claims 1-5.

30. A composition comprising an ethylene polymer and at least one other natural or synthetic polymer, wherein the ethylene polymer is characterized as:
    (A) a substantially linear ethylene/alpha-olefin polymer, or
    (B) a substantially linear ethylene homopolymer.

31. The composition of Claim 30 wherein the synthetic polymer is a conventional Ziegler polymerized ethylene/alpha-olefin polymer.

32. A fabricated article comprising an ethylene polymer, characterized in that the ethylene polymer is the ethylene polymer of any of Claims 1-5.

33. The fabricated article of Claim 32 wherein the article is:
    (A) a film, or
    (B) a fiber, or
    (C) a sheet, or
    (D) a woven fabric, or
    (E) a nonwoven fabric, or
    (F) a molded article, or
    (G) a wire and cable coating.

34. The fabricated article of Claim 33 wherein the film is a blown film.

35. The blown film of Claim 34 wherein the ethylene polymer is an ethylene/alpha-olefin copolymer having a density from 0.90 g/cm^3 to 0.92 g/cm^3.

36. The blown film of Claim 35 wherein the ethylene/alpha-olefin copolymer has a molecular weight distribution, M_w/M_n, from 1.5 to 2.5.

37. The blown film of Claim 36 wherein the film has a heat seal strength equal to or higher than a film made from a heterogeneous Ziegler polymerized polymer at the same heat seal temperature, wherein the melt index, molecular weight distribution and density of the substantially linear ethylene polymer and the heterogeneous Ziegler polymerized polymer are within ten percent of one another.

38. The process of Claim 19, wherein the polymerization comditions comprise: a temperature of from 20°C to 250°C, an ethylene concentration of from 6.7 to 12.5 percent by weight of the reactor contents, and a concentration of the substantially linear ethylene polymer of less than 5 percent by weight of the reactor contents.

39. The process of Claim 38 wherein the ethylene concentration is further characterized as not more than 8 percent of the reactor contents to form a substantially linear ethylene polymer having a I_{10}/I_2 of at least 8.

40. The process of Claim 38 wherein the ethylene concentration is further characterized as not more than 6 percent of the reactor contents to form a substantially linear ethylene polymer having a I_{10}/I_2 of at least 9.

41. The product obtainable by any one of the processes of Claims 38-40.

42. A composition comprising an ethylene polymer and at least one other natural or synthetic polymer, wherein the ethylene polymer is characterized as the substantially linear ethylene polymer of any of Claims 6-8.

43. The composition of Claim 42 wherein the synthetic polymer is a conventional Ziegler polymerized ethylene/alpha-olefin polymer.

44. A fabricated article comprising an ethylene polymer, characterized in that the ethylene polymer is the substantially linear ethylene polymer of any of Claims 6-8.

-58-

45. The fabricated article of Claim 44 wherein the article is:

(A) a film, or

(B) a fiber, or

(C) a sheet, or

(D) a woven fabric, or

(E) a nonwoven fabric, or

(F) a molded article, or

(G) a wire and cable coating.

46. The fabricated article of Claim 45 wherein the film is a blown film.

47. The blown film of Claim 46 wherein the substantially linear ethylene polymer is an ethylene/alpha-olefin copolymer having a density from 0.9 g/cm^3 to 0.92 g/cm^3.

48. The blown film of Claim 47 wherein the ethylene/alpha-olefin copolymer has a molecular weight distribution, M_w/M_n, from 1.5 to 2.5.

49. The blown film of Claim 48 wherein the film has a heat seal strength equal to or higher than a film made from a heterogeneous Ziegler polymerized polymer at the same heat seal temperature, wherein the melt index, polydispersity and density of the substantially linear ethylene polymer and the heterogeneous Ziegler polymerized polymer are within ten percent of one another.

50. The substantially linear ethylene polymer of any of Claims 6-8 wherein the substantially linear ethylene polymer is an ethylene homopolymer.

51. The substantially linear ethylene polymer of any of Claims 6-8 wherein the substantially linear ethylene polymer is an interpolymer of ethylene with at least one C_3-C_{20} alpha-olefin.

52. The substantially linear ethylene polymer of any of Claims 6-8 wherein the substantially linear ethylene polymer is a copolymer of ethylene and a C_3-C_{20} alpha-olefin.

53. The substantially linear ethylene polymer of any of Claims 6-8 wherein the substantially linear ethylene polymer is further characterized as a copolymer of ethylene and 1-octene.

-59-

54. The polymer of any one of Claims 1-8 in which the density is at least 0.87 g/cm^3.

55. The polymer of any one of Claims 1-8 in which the density is at least 0.90 g/cm^3.

56. The polymer of any one of Claims 1-8 in which the density does not exceed 0.94 g/cm^3.

57. The polymer of any one of Claims 1-8 in which the density does not exceed 0.92 g/cm^3.

58. The polymer of any one of Claims 1-8 further characterized as having a melt tension of at least 2 grams.

59. The polymer of any one of Claims 1-8 further characterized as having a processing index of less than 15 kpoise.

60. The polymer of any one of Claims 1-8 in the form of a pellet.

61. The polymer of any one of Claims 1-8 further characterized as being pelletizable at ambient temperature.

62. The polymer of any one of Claims 1-8 further characterized as being pelletizable at cool water temperatures.

63. The polymer of any one of Claims 1-8 further characterized as comprising at least one antioxidant.

64. The polymer of any one of Claims 1-8 further characterized as comprising at least one phenolic antioxidant and at least one phosphite antioxidant.
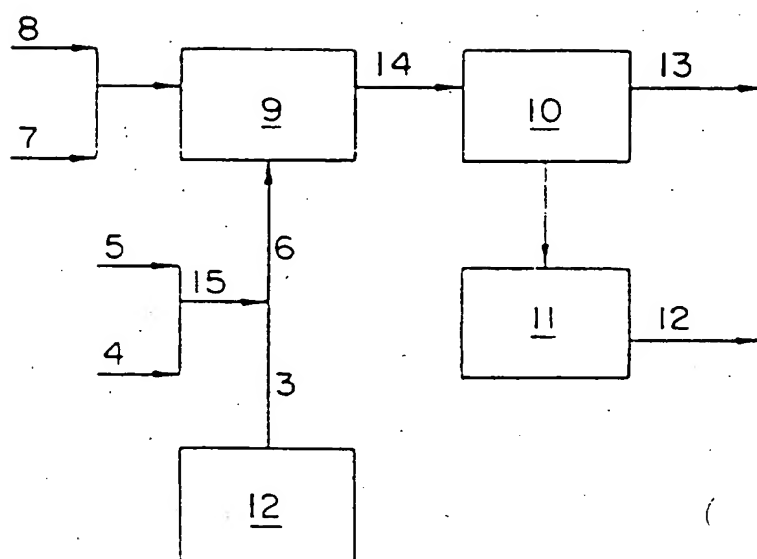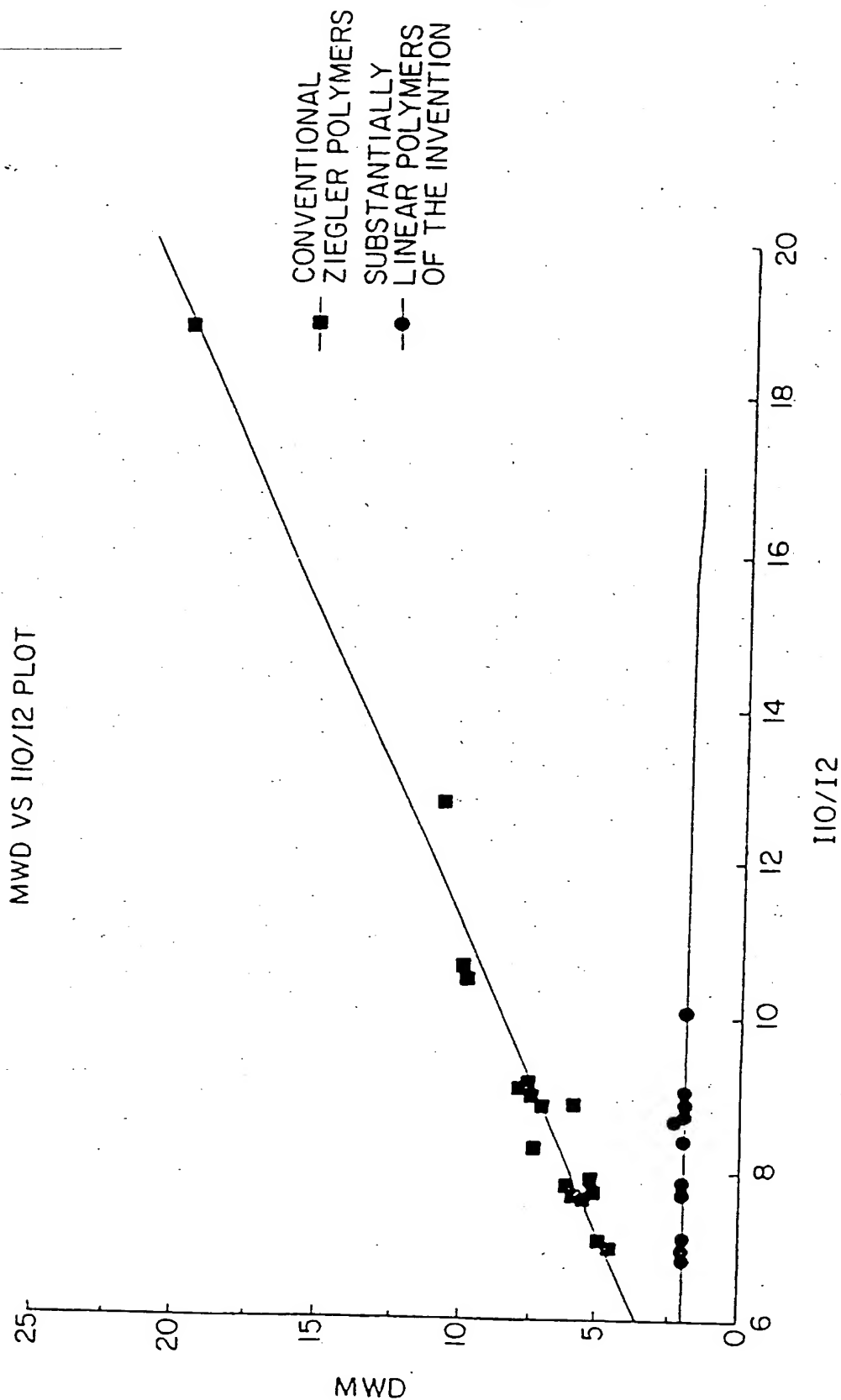
F I G. I

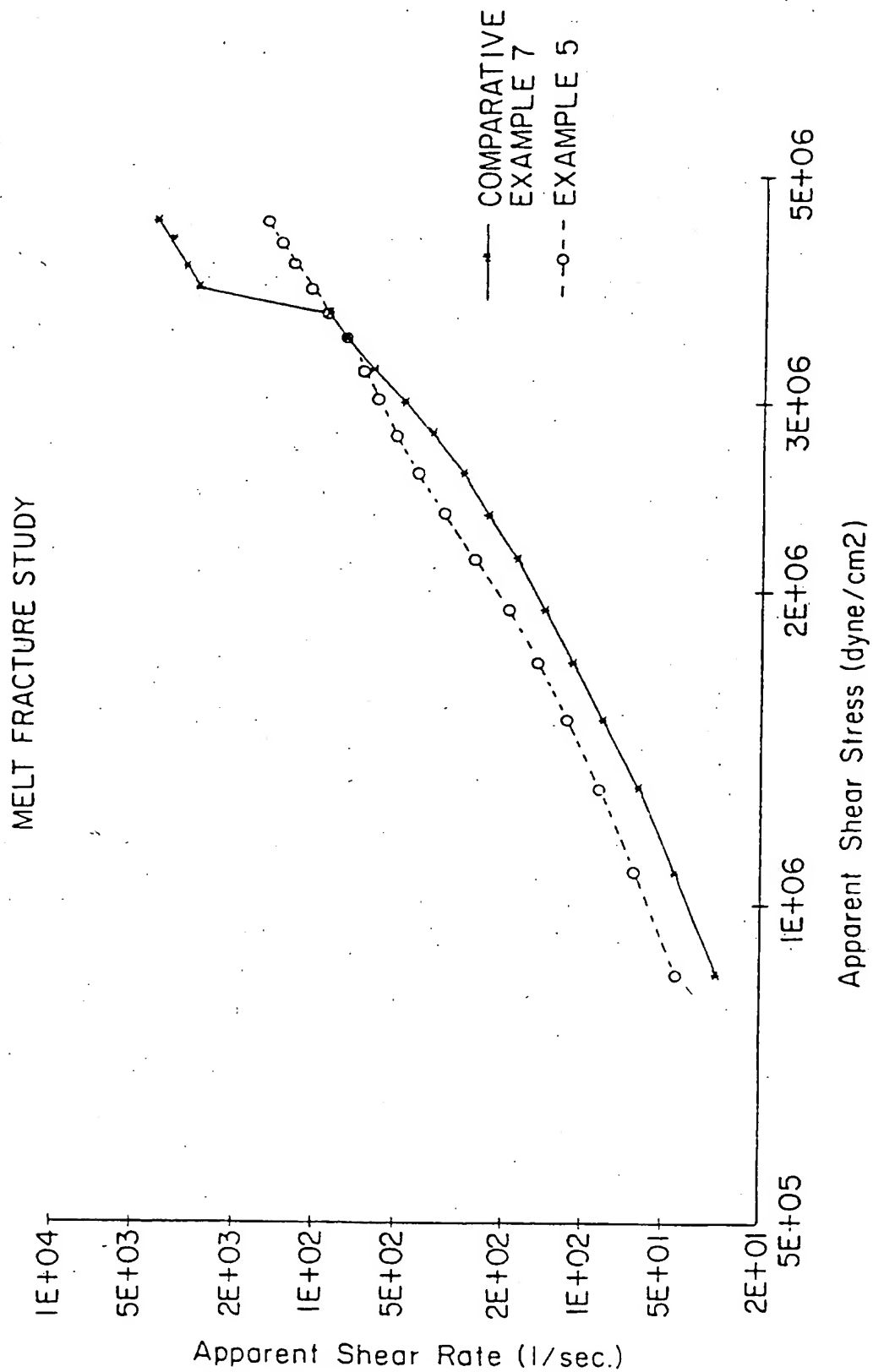MWD VS I10/I2 PLOT

CONVENTIONAL
ZIEGLER POLYMERS ■

SUBSTANTIALLY
LINEAR POLYMERS ●
OF THE INVENTION

MWD

I10/I2

F I G. 2

MELT FRACTURE STUDY

— COMPARATIVE
   EXAMPLE 7
--o-- EXAMPLE 5

Apparent Shear Stress (dyne/cm2)

Apparent Shear Rate (1/sec.)

FIG.3

MELT FRACTURE STUDY

COMPARATIVE
EXAMPLE 9
EXAMPLE 6

APPA. SHEAR RATE, I/SEC.

APPA. SHEAR STRESS, DYNE/CM2

FIG.4

HEAT SEAL PERFORMANCE COMPARISON

FIG.5

DYNAMIC SHEAR VISCOSITY

EXAMPLE 24

COMPARATIVE
EXAMPLE 26

FIG.6

Shear Rate, rad./sec.,

0.01   0.1   1   10   100   1,000

Dyna. Viscosity, poise

5,000   10,000   20,000   30,000   50,000

FIG.7

Product I10/I2

Reactor Ethylene Conc., Wt%

FIG.8

SUBSTITUTE SHEET (RULE 26)

FIG.9

LLDPE

Substantially Linear Ethylene Polymer

LDPE

Homogeneous Copolymers
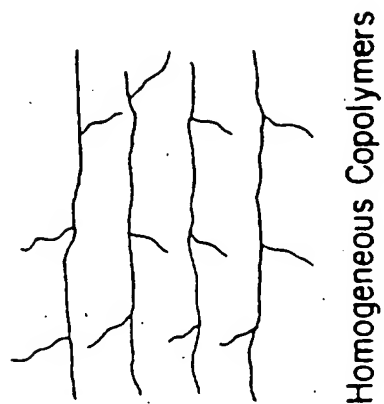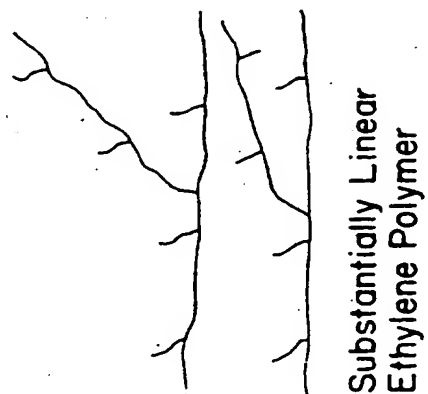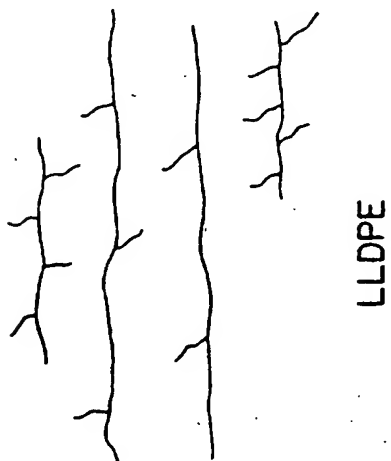
Internatic Application No

PCT/Us 95/11034

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C08F210/16   C08F4/603   C08L23/04   C08J5/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO,A,93 08221 (THE DOW CHEMICAL COMPANY) 29 April 1993 see the whole document	1-64
Y	& US,A,5 272 236 cited in the application ---	1-64
Y	WO,A,94 09060 (THE DOW CHEMICAL COMPANY) 28 April 1994 see page 18, line 16 - line 17; claims ---	1-64
A	US,A,5 241 031 (MEHTA ASPY K) 31 August 1993 see the whole document -----	1-27

[ ] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 December 1995	1 5. 01. 96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl. Fax (+ 31-70) 340-3016	Kaumann, E

Form PCT/ISA/210 (second sheet) (July 1992)

2

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9308221	29-04-93	US-A-	5272236	21-12-93
		US-A-	5278272	11-01-94
		CA-A-	2120766	29-04-93
		EP-A-	0608369	03-08-94
		FI-A-	941727	31-05-94
		JP-T-	7500622	19-01-95
		US-A-	5380810	10-01-95
		US-A-	5427807	27-06-95
		US-A-	5395471	07-03-95
WO-A-9409060	28-04-94	CA-A-	2145644	28-04-94
		EP-A-	0665863	09-08-95
		FI-A-	951799	13-04-95
		US-A-	5395471	07-03-95
US-A-5241031	31-08-93	CA-A-	2130192	02-09-93
		EP-A-	0629151	21-12-94
		JP-T-	7503913	27-04-95
		US-A-	5451450	19-09-95
		WO-A-	9316863	02-09-93